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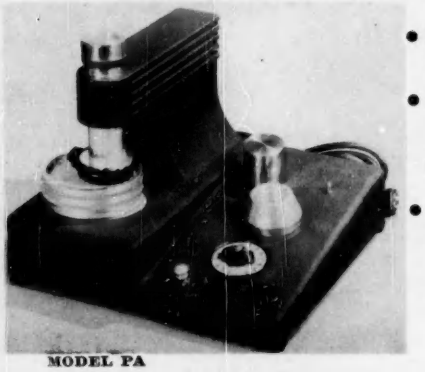

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*Mothproofing of Woolen Materials in Europe,* 1946. 28 pages, 28 photomicrographs, some in color. Price $1.50.

*Textile Microscopy in Germany,* 1950. 147 pages. Price $4.00.

*Weavability Graphs,* 1955. Sets of five graphs in large size for use by fabric designers. These graphs will take the guesswork out of design. Price $5.00.

TEXTILE RESEARCH JOURNAL

VOL. XXVII, NO. 1 JANUARY 1957

# The Plasticity of Wool

## Part III: The Physical and Chemical Causes of Variation

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**Abstract**

The variations in plasticity among the fibers of a single staple of wool have been shown to be associated with variations in swelling in water and in 100% formic acid; as a rule, fibers with the lowest plasticity (primary follicles) show the least swelling, and fibers with the highest plasticity (secondary follicles) the greatest swelling. In the great majority of cases such differences of plasticity and swelling do not seem to be governed by differences in sulfur content, i.e., in the degree of cross-linking with cystine. They are, however, dependent on the relative proportions of accessible (amorphous) and inaccessible (crystalline) material in the fibers, the proportions of accessible material being deduced from the gain in dry weight of the fibers after exposure to $D_2O$. Fibers showing the highest plasticity and swelling contain the greatest proportion of accessible material, and *vice versa*. Further, fibers of high plasticity contain more tyrosine than fibers of low plasticity, suggesting that the bulky side chains of tyrosine are one cause of main chain disorder in wool, just as in the case of silk.

The above observations have an important bearing on the assessment of wool quality. Using 20 Cape merino wools, which had been classified as good, ordinary, or common in quality by expert appraisers in South Africa, it has been shown that the good quality wools have the highest plasticity, even when comparison is restricted to groups of fibers of similar thickness. Since the behavior of wool at various stages of processing is determined to some extent at least by the plasticity of the fibers, and since there is no necessary connection between plasticity and fineness of fiber, it must be concluded that the quality of wool cannot be defined in terms of dimensional characteristics alone. Not until breeding policy is based on knowledge of the substance of fibers as well as of their dimensions can there be any precise and effective link between the producer and user of wool.

IN previous papers it has been shown that the wide variations in plasticity among the fibers of a single staple of wool [7] are associated with the types of follicle from which the fibers are derived [1]. Primary follicles were found to produce fibers of lower plasticity than those from secondary follicles, and the order of plasticity of fibers of different types is, in general, the inverse of the order of development of the follicles. From first principles it seemed probable that the plasticity of wool would decrease with

increasing sulfur content, i.e., with increasing number of cystine cross-linkages between neighboring peptide chains, and a relationship of this kind was observed with the first wool to be examined [7]. The range of plasticity exhibited by this wool has since been shown to be abnormally wide, and much smaller variations in sulfur content were noted among fibers from different types of follicle in the case of New Zealand Romney wool [2]. It thus became clear that many more wools would have to be examined before the influence of the extent of cystine cross-linking on the plasticity of wool could be defined. A second possible cause of variations in plasticity is variations in crystalline/amorphous ratio, since molecular unfolding in the ordered regions of the fiber will proceed more slowly than in the disordered regions. A study of these two possible causes of variations in plasticity was, therefore, undertaken as soon as the biological origin of the variations had been established.

## Experimental Procedures

### *Selection of Wools*

Seven hogget wools, representing a range from crossbred to pure merino wools grown in different localities in Australia, New Zealand, and South Africa, were selected for use in studying the relationship between plasticity, as determined by the type of follicle from which the fibers were derived, and swelling properties, sulfur content, and crystalline/amorphous ratio, the swelling of the fibers in different media being measured to give a general indication of the cohesion of the structure.

For later studies of the relationship between plasticity and wool quality, Cape merino wools were obtained from the Grootfontein College of Agriculture, one group having been shorn in 1951 and the other in 1954. Samples of 50 of the 1951 wools were submitted to four experts for judgment of spinning quality, quality, and condition. South African wool growers usually differentiate between three qualities, viz., good, ordinary, and common [8], and there was good agreement between the experts in the appraisal of 12 of the 50 wools. These 12 were, therefore, used in the present experiments. The 1954 wools, which, like the 1951 wools, had been grown under "veld" or pasture conditions, were submitted for appraisal to only one of the four experts who had assessed the 1951 wools, and 8 of the wools were selected for examination.

### *Purification of Wools*

Each sample of wool was purified by extraction for 24 hr. each with ether and alcohol in a Soxhlet apparatus. After being washed in frequent changes of distilled water over a period of 24 hr., the wool was finally pressed between filter papers and allowed to dry in room air.

### *Selection of Fiber Types*

The fibers were sorted into fiber types according to Dr. F. W. Dry's system of classification for hogget wools by laying the staple of wool on a black velvet cloth, withdrawing individual fibers with forceps, and, in the case of New Zealand Romney wools, classifying them as sickles, early curly-tips, late curly-tips, and long and short histerotrichs. The early and late curly-tips of merino wools were grouped together as curly-tips, and the long and short histerotrichs also were not separated. Sorting was continued until a 0.15-g. sample of each type of fiber was obtained.

### *Plasticity*

Plasticity measurements were carried out in distilled water at 22.2° C., using a load of 700 kg./cm.$^2$, under the same conditions as before [1].

### *Swelling*

Six fibers were selected at random from each of the groups of fibers. A 6-cm. (approx.) length of each fiber, taken from the root end, was mounted on a microscope slide in such a way that slight length contraction was possible, the ends of the fiber being anchored with picien wax. As a rule, four fibers of different types were mounted in parallel on each slide in order to ensure strictly comparable results, the fibers being protected then with a cover slip, which was attached to the slide with picien. After the fibers had been conditioned for 24 hr. in the humidity room (65% R.H., 22.2° C.), their widths were measured under the microscope at 2-mm. intervals along the length, the measurements being made where the fibers crossed a series of lines, which had been engraved at right angles to the length of the slide, in order to ensure complete impartiality of observation. The slide was then flooded with distilled water, which was made to flow over the fibers by adding the water at one end of the cover slip and absorbing it at the other end with filter paper. After

the fibers had been soaked for at least 30 min. at 22.2° C., measurements of width were made in the same way as before. Without removing the cover slip, the fibers were again conditioned in the humidity room before applying formic acid (100%) in the same way as for the preceding measurements in water, the formic acid having been shown to contain less than 0.1% of water by testing with the Karl Fischer reagent [4]. The fibers were immersed in the acid for at least 20 min. at 22.2° C. before measurements of width were made. During treatment with formic acid, wool fibers contract slightly, and it was for this reason that they were mounted slightly slack in the first instance.

*Sulfur Content*

Because so much labor is involved in classifying fibers of different types, and since only a small amount of material was available in each case, Dr. G. Weiler of the Microanalytical Laboratory, Oxford, very kindly agreed to carry out the sulfur determinations himself, as was the case with the two sets of sulfur determinations mentioned in the introduction to this paper.

*Crystalline/Amorphous Ratio*

It has been shown in a previous paper [2] that different forms of keratin are placed in the same order, as regards crystallinity, by the Hailwood-Horrobin analysis of the water-adsorption isotherms [5] and by determinations of the gain in dry weight after exposure to saturated heavy water vapor ($D_2O$). Besides being less laborious, the second procedure is believed to give more reliable values for the fraction of keratin which is accessible to $D_2O$, this fraction being calculated by expressing the observed gain in dry weight as a fraction of the theoretical increase, calculated from the amino acid analysis on the assumption of complete accessibility to $D_2O$. The increases in dry weight of the various fiber types in different wools were determined in the usual way [2], and the theoretical increase was again assumed to be 1.615%. More precise values for the theoretical increase can now be derived from recent complete analyses of merino wools [3, 9], but the older value is retained for the sake of simplicity in comparing old and new data, especially as exact definition of the fraction accessible is impossible until the compositions of accessible and inaccessible fractions are known.

*Tyrosine Content*

The tyrosine contents of single fibers of different types were compared by the method which has been described in a previous paper [6]. Fibers selected from two New Zealand Romney wools were used. After the plasticity constants of 24 early curly-tips and 24 long histerotrichs from each wool had been determined in the usual way, except that the load was removed when an extension of 50% had been reached, the fibers were allowed to rest in distilled water for at least 72 hr. From these fibers the eight with the lowest plasticities were selected from the early curly-tips and the eight with the highest plasticities from the long histerotrichs. The fibers were then iodinated for 90 hr. at 25° C. with a solution of iodine in absolute alcohol. This solution was prepared as follows.

A solution (1.3 ml.) of $^{131}I$, with an activity of 10 milli-curies, was transferred to a small centrifuge tube and made up to 2 ml. with distilled water. A few drops of sulfuric acid ($5N$), and a freshly prepared saturated solution of potassium iodate (0.5 ml.) containing sulfuric acid (10 ml./liter), were then added with stirring. As there was not enough iodide present to precipitate the iodine, a solution of potassium iodide (5 ml., 2.5%) was added so that the precipitated iodine would act as a carrier for the $^{131}I$. Precipitation of the iodine was completed by further additions of the solution of potassium iodate. The iodine was collected and purified by centrifugation and washing with distilled water, before being dried with filter paper and made up to 2 ml. with absolute alcohol.

The fibers were iodinated in groups of four in 1 ml. of the solution in a 1-ml. tube provided with a ground glass stopper. After treatment, the fibers were washed 20 times with absolute alcohol, freed from loosely bound iodine by treatment with sodium thiosulfate solution (40 ml., $0.1N$) for 48 hr., and then washed with frequent changes of distilled water over a period of 3 days. The four fibers were then mounted in parallel under low tension across a metal frame. Small pieces of iodinated fiber were tied round each fiber at the ends to act as reference points, and the width of the fibers was measured at 1-mm. intervals between the reference points in an atmosphere at 65% R.H. and 22.2° C. Finally, the fibers were placed between two N 40 Ilford Process plates for 20 min. After the plates had

been developed, the intensity of the blackening was measured at 1-mm. intervals between the reference points with a photometer. In this case the blackening of the plates was measured directly. As the image was traversed across the source of light, from one edge to the other, the blackening increased slowly to a maximum and then decreased. The average of the maximum readings along the length of the fiber gives a measure of the tyrosine content, corrections being, of course, applied for differences in width so that the results for different fibers can be compared. It should, however, be noted that the results for different types of fiber can be compared only in pairs (Table III), because the half-life of $^{131}I$ is short and the iodinations were carried out at different times. The results given in Table III are

**TABLE I**

| Type of fiber | Plasticity measurements: No. of fibers | Plasticity measurements: Average fiber width ($\mu$) | Plasticity measurements: Average value of $k$ ($\times 10^{-5}$) | Sulfur content (% on dry weight) | Fraction accessible (%) | Width swelling (%) in: $H_2O$ | Width swelling (%) in: H·COOH |
|---|---|---|---|---|---|---|---|
| 1. New Zealand Romney Hogget Wool (covered during growth) (Values of $k$ based on a limiting extension of 75%) | | | | | | | |
| Sickles | 11 | 29.2 | 57.5 | 3.26 | — | 12.4 | 53.8 |
| E.C-T. | 10 | 39.9 | 48.6 | 3.44, 3.30 | 76.8 | 8.2 | 53.5 |
| L.C-T. | 12 | 39.4 | 48.6 | 3.38, 3.40 | 78.6 | 7.2 | 52.6 |
| L.H. | 12 | 30.8 | 68.0 | 3.20, 3.20 | 81.7 | 14.0 | 59.6 |
| S.H. | 12 | 23.9 | 68.5 | 3.48, 3.72 | 84.2 | 14.0 | 62.3 |
| 2. New Zealand Romney Hogget Wool (covered during growth) (Values of $k$ based on a limiting extension of 70%) | | | | | | | |
| Sickles | 11 | 36.0 | 78.7 | — | — | 7.8 | 54.3 |
| E.C-T. | 12 | 39.3 | 79.9 | — | 79.9 | 8.2 | 56.1 |
| L.C-T. | 11 | 36.3 | 98.7 | — | 82.4 | 10.2 | 57.1 |
| L.H. | 13 | 31.4 | 108.2 | — | 81.1 | 14.7 | 59.9 |
| S.H. | 6 | 25.4 | 137.5 | — | 86.7 | 16.3 | 64.3 |
| 3. Australian Merino Lamb's Wool (70s quality, 6 months' growth) (Values of $k$ based on a limiting extension of 70%) | | | | | | | |
| Sickles | 7 | 19.9 | 88.4 | — | — | 6.9 | 50.5 |
| E.C-T. | 5 | 23.6 | 107.2 | 2.98, 3.01 | 87.3 | 8.1 | 54.3 |
| L.C-T. | 7 | 20.8 | 133.3 | | | 8.6 | 55.0 |
| H. | 6 | 17.3 | 167.6 | 2.96, 2.97 | 88.5 | 18.3 | 70.3 |
| 4. Natal (S.A.) German Merino × Merino Crossbred Lamb's Wool (7–8 months' growth) (Values of $k$ based on a limiting extension of 70%) | | | | | | | |
| Sickles | 4 | 15.3 | 138.0 | — | — | 9.1 | 48.6 |
| C.-T. | 6 | 20.8 | 138.1 | 3.20, 3.13 | 86.1 | 7.2 | 55.0 |
| H. | 3 | 16.9 | 227.4 | 3.41, 3.17 | 89.8 | 16.6 | 67.2 |
| 5. Glen (Bloemfontein, S.A.) Merino (10–12 months' growth) (Values of $k$ based on a limiting extension of 80%) | | | | | | | |
| C-T. | 8 | 17.0 | 65.2 | 3.54, 3.50 | 84.2 | 9.2 | 53.2 |
| H. | 8 | 16.1 | 65.7 | 3.32, 3.38 | 83.0 | 16.3 | 62.4 |
| 6. Grootfontein (S.A.) Merino (9 months' growth) (Values of $k$ based on a limiting extension of 80%) | | | | | | | |
| C-T. | 10 | 22.6 | 103.7 | 3.24, 3.18 | 86.7 | 10.4 | 52.4 |
| H. | 6 | 16.2 | 114.8 | 3.39, 3.24 | 88.5 | 13.5 | 67.3 |
| 7. Grootfontein (S.A.) Merino (9 months' growth) (Values of $k$ based on a limiting extension of 80%) | | | | | | | |
| C-T. | 8 | 22.3 | 122.5 | 3.46, 3.22 | 86.7 | 10.0 | 54.0 |
| H. | 8 | 16.8 | 181.0 | 3.44, 3.46 | 89.2 | 15.5 | 64.8 |

expressed as $100W/d^2$, where $W$ is the average blackening caused by the fiber and $d$ is its width in arbitrary units (divisions of the eyepiece micrometer).

## Results

### (*a*) *Comparison of Fiber Types*

See Table I for results.

### (*b*) *Comparison of Wools of Different Quality*

In this case a single staple was taken at random from each sample of wool, and after the tip had been cut off, a bundle of about 30 fibers was taken from the inside of the undamaged root portion with forceps. After purification, 24 of the fibers were used for plasticity determinations. Many of the fibers broke at extensions too low to permit precise calculation of plasticity, and it was, therefore, decided to compare the plasticities of fibers of similar diameter from the good, ordinary and common qualities of wool. The results are given in Table II.

**TABLE II**

| Fiber width ($\mu$) | Plasticity ($k$) of fibers from wools characterized as ($\times 10^{-5}$) | | |
|---|---|---|---|
| | Good | Ordinary | Common |
| < 19.0 | 111.6 (26) | 86.4 (5) | 86.5 (7) |
| 19.0–20.0 | 108.5 (22) | 82.9 (15) | 103.4 (12) |
| 20.1–21.3 | 94.2 (17) | 72.5 (21) | 85.7 (12) |
| 21.4–23.0 | 87.2 (11) | 85.0 (21) | 71.2 (11) |
| > 23.0 | 82.1 (14) | 85.6 (46) | 66.5 (52) |
| Avg. (per fiber) | 100.0 | 82.5 | 75.7 |

Values of $k$ are based on a limiting extension of 80%.
The figures in parentheses are the numbers of fibers examined.

**TABLE III**

| Early curly-tips | | | Long histerotrichs | | |
|---|---|---|---|---|---|
| Fiber width ($\mu$) | $k$ ($\times 10^{-5}$) | $100W/d^2$ | Fiber width ($\mu$) | $k$ ($\times 10^{-5}$) | $100W/d^2$ |
| New Zealand Romney Wool (Values of $k$ based on a limiting extension of 70%) | | | | | |
| 37.2 | 41.2 | 6.9 | 31.8 | 74.9 | 8.4 |
| 40.4 | 58.7 | 6.1 | 28.4 | 68.0 | 10.3 |
| 36.5 | 55.5 | 7.7 | 28.3 | 68.2 | 9.3 |
| 41.5 | 50.5 | 6.8 | 24.7 | 94.5 | 11.8 |
| 38.2 | 51.5 | 5.6 | 26.5 | 100.7 | 8.3 |
| 37.8 | 48.0 | 6.2 | 27.0 | 68.0 | 9.9 |
| 42.7 | 49.2 | 4.8 | 28.9 | 81.4 | 7.4 |
| 37.8 | 43.2 | 4.8 | 31.7 | 67.7 | 6.2 |
| | | Avg. = 6.1 | | | Avg. = 9.0 |
| | | sd = 1.0 | | | sd = 1.7 |
| | | cv = 16.0% | | | cv = 18.4% |
| | | se = 0.4 | | | se = 0.6 |
| New Zealand Romney Wool (Values of $k$ based on a limiting extension of 75%) | | | | | |
| 42.3 | 29.5 | 6.6 | 25.1 | 65.5 | 14.4 |
| 43.8 | 30.5 | 5.1 | 31.8 | 63.5 | 9.4 |
| 38.9 | 27.5 | 5.9 | 30.0 | 82.0 | 8.5 |
| 37.9 | 29.7 | 5.4 | 29.3 | 72.7 | 7.7 |
| 45.5 | 31.9 | 6.1 | 27.4 | 63.4 | 12.0 |
| 35.1 | 28.3 | 9.2 | 26.1 | 64.4 | 15.0 |
| 41.7 | 26.7 | 6.2 | 28.4 | 66.9 | 10.1 |
| 40.2 | 25.7 | 6.7 | 32.6 | 62.4 | 10.4 |
| | | Avg. = 6.4 | | | Avg. = 10.9 |
| | | sd = 1.2 | | | sd = 2.5 |
| | | cv = 18.4% | | | cv = 22.6% |
| | | se = 0.4 | | | se = 0.9 |

(*c*) *Comparison of the Tyrosine Contents of Fibers of Different Types*

See Table III for results.

## Discussion of Results

As regards the plasticity of fibers of different types, the results given in Table I confirm those of the preceding paper [1] in this series; in general, the first follicles to develop produce fibers with the lowest plasticity, and *vice versa*. Such differences in plasticity are associated with differences in swelling in water and in formic acid. As a rule, the order in which the fibers are placed as regards swelling in either medium is the order of development of the follicles, and fibers from the late secondary follicles invariably swell to a far greater extent than fibers from primary follicles, especially in formic acid. But the extent to which a fiber swells is determined by two opposing factors, viz., the swelling pressure, which is developed by combination with the swelling medium, and the cohesion of the fiber structure, which resists swelling. Since the water-adsorption and acid-combining capacities of different wools are so similar, there can be little doubt that the different degrees of swelling of fibers from different types of follicle are due to differences in cohesion of the keratin.

The differences in cohesion with which differences in plasticity are associated may arise in several ways. Of these the first to be considered was variations in sulfur content, i.e., in the degree of cross-linking with cystine. It is clear from the results of Table I that the first wool to be examined [7] (English Lincoln) was exceptional, not only in range of plasticity, but also in giving an inverse relationship between plasticity and sulfur content (with fibers classified in order of plasticity without reference to their origin). When fibers are classified according to the type of follicle from which they are derived, as in Table I, the variations in plasticity are clearly independent of variations in sulfur content, which are small, with each of the six wools for which both sets of data are available.

Attention was next turned to the possibility that the differences in plasticity and cohesion between fibers from different types of follicle might be due to differences in the proportions of ordered (crystalline) material in the fibers. Some indication that the least plastic fibers (from primary follicles) contain a higher proportion of ordered material than the most plastic fibers (from secondary follicles) has already been obtained in the case of New Zealand Romney wool [2]. With very few exceptions, this observation is confirmed by the data for the fraction accessible to $D_2O$ of the various types of fiber present in the seven wools of Table I. It is, however, surprising that the range of values for the accessible fraction should be so small in comparison with the wide variations in plasticity and swelling. The possibility that the ordered regions of the fiber are not totally impermeable to $D_2O$ cannot be ignored, and Linderstrom-Lang's studies of hydrogen-deuterium exchange in the case of insulin demonstrate that the case of exchange with peptide bonds depends on their chemical environment; in particular, the hydrogen atoms of the peptide bonds within the loop formed by the bridging of the two chains by two cystine bonds are generally more slowly exchangeable than those of peptide bonds outside the loop, those of the side chains being instantaneously exchangeable. Although a more detailed examination of the rate of replacement of hydrogen by deuterium in keratin is, therefore, to be undertaken, it should be emphasized that the present experiments, in which keratin was exposed to $D_2O$ for 2 to 3 days, do place different wools and mohair in the same order, as regards crystallinity, as the Hailwood-Horrobin analysis of the water-adsorption isotherms [5]. A sharper discrimination between different types of fiber, as regards crystallinity, may be possible with shorter times of exposure to $D_2O$, especially at low temperatures, but the results under discussion do indicate that high swelling and plasticity are associated with a high proportion of amorphous (accessible) keratin in the fibers. Further, since the more plastic fibers (histerotrichs) of the two New Zealand Romney wools (Table III) contain a greater proportion of tyrosine than the less plastic fibers (early curly-tips), bulky side chains seem to be one cause of main chain disorder in keratin, just as in the case of silk.

The significance of these results in relation to wool quality may be deduced from the properties of the Cape merino wools of good, ordinary, and common quality. From the histograms of Figure 1, which illustrate the distribution of fibers of different plasticity for the three types of wool, it is evident that plasticity tends to decrease as the quality decreases. Even when fibers of similar thickness from

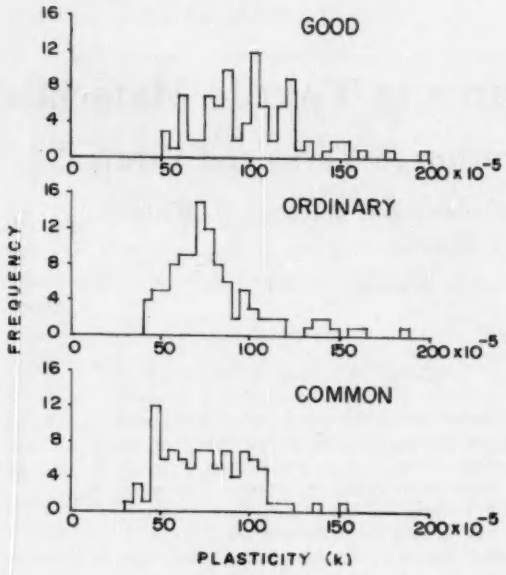


**Fig. 1.**

the three qualities are compared, as in Table II, it is again evident that fibers from good quality wools are higher in plasticity than those from ordinary and common qualities, though there is no sharp distinction between fibers from ordinary and common qualities. These results suggest, therefore, that wools of high plasticity are preferred by expert appraisers in South Africa, the differences in plasticity being detected, presumably, by subtle differences in handle. It must be concluded, therefore, that the quality of wool is not determined solely by the dimensional characteristics of the fibers, important though these characteristics are. The tacit assumption that differences in the substance of different wools are either without effect on quality, or that differences in substance are paralleled by differences in fiber thickness, is clearly unfounded. Further, since differences in substance are closely associated with differences in plasticity, and since the behavior of wool at different stages of processing, e.g., in the storage of tops prior to spinning, in the storage of yarn prior to weaving, and in the finishing of cloth, is dependent on the plasticity of the fibers, it seems reasonable to conclude that experts with long industrial experience are able to predict the behavior of a wool during processing from its appearance and feel. In the same way they are able to select from among wools of similar fineness those which are best suited to the manufacture of particular types of fabric. These more subtle aspects of the assessment of wool quality have so far proved to be incapable of exact measurement, and it has, therefore, been impossible for the manufacturer to define for the grazier exactly what characteristics he desires in wools which are to be used for different purposes. The preceding experiments do, however, suggest that such guidance might be obtained if, besides defining dimensional characteristics, account is also taken of the differences in substance which affect plasticity. Measurement of plasticity is itself too tedious for routine use, but the related crystallinity can be readily assessed by determining the gain in dry weight of wool after exposure to $D_2O$ under standard conditions, which need not be those adopted in this investigation. Routine determinations of the crystallinity of the fleeces of rams, in association with the usual definition of the dimensional characteristics of the fibers, should allow all aspects of wool quality to be brought under control, and should provide the precise link between the producer and the user of wool which has been so long desired.

### Acknowledgment

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# Water Transport Mechanisms in Textile Materials[1]

## Part II: Capillary-Type Penetration in Yarns and Fabrics[2]

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**Abstract**

In view of the interest in the phenomenon of "wicking" in apparel fabrics made of synthetic fibers or of blends, a basic study of the mechanism of water transport in yarns and fabrics has been made. The movement of water along fabrics is shown to depend on the laws of capillary action. Because the rates of travel of water in many fabrics and in yarns from these fabrics are approximately equal, it is concluded that water is carried mainly in the capillaries formed by the fibers in the individual yarns. The speed of travel of water in these capillaries is readily reduced by the presence of randomly arranged fibers in the yarn, and it is this factor rather than the nature of the fiber material which accounts for the wide range of water transport properties found in blended fabrics. The rates at which drops of water placed on the surface of such fabrics are absorbed also appear to depend on the same principles. However, for the fabrics that have been studied, these are considerably lower in magnitude than the rates for water travel within the fabrics. Since the water-holding capacities of fabrics made of different fiber materials in a similar construction are also similar, the amount of water carried by a fabric in a rate experiment depends mainly on the capillary laws which define the distance of travel in unit time. The rate of travel of water in a group of wool-type blended fabrics can be correlated with their thermal resistance properties, and both appear to depend on the arrangement of the individual fibers in the fabrics. Random arrangement of the fibers in the yarns leads to fabrics along which water travels slowly and which possess increased thermal insulation in the moist state. The water transport properties of fabrics in general provide useful information about fiber arrangement in fabrics and yarns, and it appears that the rather simple drop absorption technique for surface wetting can be conveniently used for this purpose in studying wool-type fabrics.

### Introduction

The observation that liquid water moves more readily through fabrics of high synthetic fiber content than through similar all-wool fabrics has been widely noted. This so-called "wicking" behavior has been shown to be mainly a reflection of differences in the yarn structure of the fabrics rather than differences in the chemical nature of the fibers [5]. Water transport in yarns occurs through the capillaries formed by the individual fibers. Hence, the rate of travel of liquid water is governed by the fiber arrangement factors in yarns which control capillary size and continuity. The over-all case of wetting of the yarn is strongly influenced by the roughness of the yarn surface, and it is this factor, rather than fiber wettability, which controls the rate of water transport in many blended yarns and fabrics.

The present discussion is concerned with water travel in fabrics varying in fiber type and fabric construction. The rate of water travel in fabrics is analyzed in terms of their water-holding capacity, ease of wetting of the surface, and the water transport properties of the yarns. The thermal insulating value of several "wool-type" blended fabrics and the arrangement of fibers in these fabrics are also considered in terms of their yarn structure and water transport properties.

[1] This work constitutes a part of the Army Quartermaster program of research on warmth and comfort of military fabrics, performed under contract QM 564.

[2] Part I appeared in TEXTILE RESEARCH JOURNAL **26**, 829 (1956).

## Experimental

The rate of water transport along a fabric was evaluated by placing a strip 1 in. wide, 3½ in. long, horizontally over an electrical contacting device and by following the motion of water along the fabric with time. Although methods have been developed for following water traveling vertically in fabrics [2] and paper [4], the mathematical analysis of the transport rate is simpler in the horizontal capillary penetration process [6] since gravity effects are absent.

In the horizontal water transport apparatus, illustrated in Figure 1, the fabric is held on pairs of contact pins, and one end dips into a small beaker of water. The water level in the beaker is measured with the attached manometer so the volume of water transferred to the fabric can be obtained. For the apparatus of Figure 1, the contact pins were placed at 2 cm., 1 cm., ½ cm., and ½ cm., starting from the end nearest the beaker. Movement of water along the fabric to each set of contacts triggered a buzzer, and so the distance of water travel as a function of time could also be determined.

A method was devised for determining the water-holding capacity of the fabric strips used in the water transport apparatus. The convention of allowing one minute of drainage from the strips held in a horizontal position was found to duplicate most closely the wetness achieved in the rate experiments. The resulting water-holding capacity values were calculated on the basis of the conditioned weights of the fabric samples, i.e., in an atmosphere of 70° F. and 65% relative humidity.

The surface wetting properties of the fabrics were determined by a "drop absorption" technique. A 0.2-ml. drop of distilled water was placed carefully on the fabric surface and covered with a petri dish to prevent variations due to uncontrolled air movement. The time taken for the mirrorlike reflecting properties of the drop to disappear was adopted as the drop absorption time.

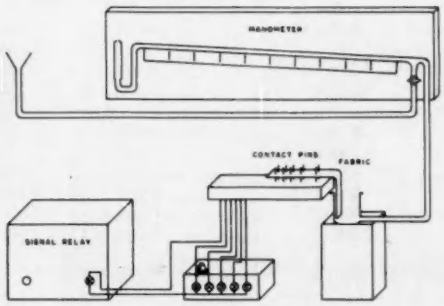


FIGURE 1. THE HORIZONTAL WATER TRANSPORT APPARATUS

The water transport properties of yarns taken from the fabrics and their contact angles with water were determined by the methods previously described [5].

## Water Transport Equations for Fabrics

It has been shown [5] that, in general, the travel of liquid water through textile fiber assemblies is governed by the capillary penetration rate expression

$$s^2 = \frac{\gamma \cos \theta_A' r_c t}{2\eta} = k_s t \qquad (1)$$

in which $s$ is the distance traveled by a liquid of surface tension $\gamma$, and viscosity $\eta$, through capillaries of effective radius $r_c$, in time $t$. The capillaries are wet at an apparent advancing contact angle $\theta_A'$, and so the rate constant $k_s$ represents penetration for a given liquid into a specific assembly of fibers. Accordingly, a plot of the square of the distance of water travel against time is linear with the slope $k_s$, the water transport rate constant, with dimensions of cm.²/sec.

The amount of water transported by a fabric depends on its water-holding capacity and on the rate with which water travels through the fabric. If the water-holding capacity per unit area of fabric at saturation is $m_w$ grams, then the rate of water transport in terms of the amount of water transported is

$$k_m = m_w^2 k_s \qquad (2)$$

where the units of $k_m$ are g.²/cm.² sec. Accordingly, the rate equation for the amount of water transported, $m$, is

$$m^2 = m_w^2 \frac{\gamma \cos \theta_A' r_c t}{2\eta} = k_m t \qquad (3)$$

The magnitude of the water-holding capacity $m_w$ has been shown to depend almost entirely on fabric construction [3] and, for fabrics of similar construction, mainly on fabric thickness. The value of the water transport rate constant $k_s$ thus depends on these fabric properties as well as on the apparent contact angle $\theta_A'$ and the effective capillary radius $r_c$.

Water transport data obtained by the horizontal strip method on several contrasting fabric types are

given graphically as the square of the distance traveled versus time in Figure 2. The water transport curves are linear, as predicted by Equation 1, and have slopes representing the water transport rate $k_s$ for each fabric. However, not all of the curves pass through the origin, suggesting that the experimental rates could be represented more exactly by the expression

$$s^2 = k_s(t - t_s) \qquad (4)$$

in which $t_s$ is a constant for each fabric. This constant, representing an initiation period before the main capillary process could occur, appeared to be related to the time required for the water to penetrate the surface of the yarns and fabrics. This hypothesis was tested by comparing the results from drop absorption with those from water transport.

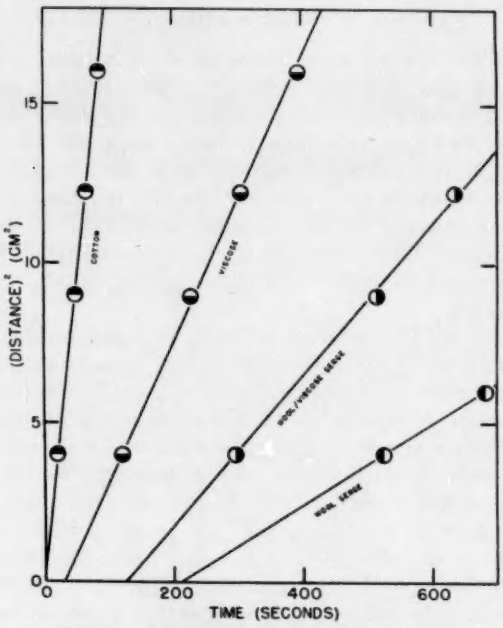


FIGURE 2 "DISTANCE" WATER TRANSPORT CURVES FOR SEVERAL FABRIC TYPES

## Surface Wetting and Water Movement in Fabrics

Fabrics containing a number of fiber types, including blends with wool, mainly in serge and knit underwear constructions, were examined by the various water transport techniques. Results of these experiments are summarized in Table I.

The drop absorption time values can be compared with the $t_s$ values for each fabric from the data in

**TABLE I. A Comparison of Surface Wetting and Water Transport in Fabrics**

| Sample no. | Description | Surface wetting by: Drop absorption (sec.) | Surface wetting by: Rate curve intercept, $t_s$ (sec.) | Water transport: Rate (cm.²/sec.) | Water transport: 1-in. travel time* (sec.) |
|---|---|---|---|---|---|
| 27 | 100% Cotton twill | 1 | 4 | 0.19 | 35 |
| E | 100% Cotton herringbone | 3 | 16 | 0.17 | 37 |
| 48 | 100% Cotton serge | 3 | 18 | 0.16 | 41 |
| 68 | 100% Cotton underwear | 5 | 26 | 0.20 | 32 |
| $N_2$ | 100% Nylon serge | 10 | 65 | 0.18 | 36 |
| 70† | 100% Wool underwear | 180 | 510 | 0.029 | 220 |
| 62 | 100% Nylon underwear | 330 | 590 | 0.016 | 400 |
| 20 | 100% Orlon‡ serge | 1050 | 1760 | 0.010 | 1380 |
| A | 100% Wool serge | 8500 | 1720 | 0.003 | 2150 |
| 741 | 70/30 Wool/Orlon serge | 330 | 155 | 0.057 | 115 |
| 743 | 70/30 Wool/Orlon serge | 350 | 160 | 0.043 | 150 |
| 742 | 70/30 Wool/Dacron§ serge | 350 | 320 | 0.038 | 170 |
| 8 | 65/35 Wool/Orlon serge | 1020 | 200 | 0.033 | 195 |
| 28 | 50/50 Wool/Orlon serge | 1480 | 1090 | 0.007 | 900 |
| 26 | 70/30 Wool/Orlon serge | >16000 | 2740 | 0.005 | 1470 |

* Time required for water movement along the first inch in the fabric plane, calculated from the water transport rate.
† Sample treated to make it wettable.
‡ Du Pont acrylic fiber.
§ Du Pont polyester fiber.

columns 3 and 4. While there is by no means complete correlation, the two methods rank the surface wetting properties of the fabrics in nearly the same order and, accordingly, $t_s$ has been termed the "surface wetting time" for each fabric. This permits a direct interpretation of the fabric horizontal water transport curves represented by Equation 4. The delay in water travel along the fabric, indicated by intercepts of the curves of Figure 2 on the time axis, is a direct result of the fact that it takes relatively longer for the water to penetrate the fabric surface than to move in the interior. This can be seen in another way by comparing the time taken for the water to move the first inch in the fabric interior (column 6) with the drop absorption time. In general, the time required for movement of water 1 in. in the direction of the fabric plane (once the end of the fabric is wet) is similar in magnitude to the time required for water to penetrate the fabric surface, a distance certainly no greater than 0.020 to 0.030 in. Accordingly, it seems likely that surface wetting and water travel in the fabric interior are controlled by the same fabric properties, and these will be discussed in more detail in a later section of the paper. It does appear that the relatively simple water absorption test can be used to estimate the capillary-type penetration properties for these types of fabrics.

## Water Transport in Yarns Taken from Fabrics

Water transport experiments were carried out on a number of different fabric types and on the two-ply yarns taken from these fabrics. The water transport rates for these fiber assemblies, calculated using Equations 4 and 1, are given in Table II. It can be seen that for all of the fabrics examined, the yarn and fabric rates for each material were quite similar. Apparently water travel in the yarns accounted for virtually all of the motion of water in the parent fabrics. Thus, the effects of change in yarn twist, fiber denier, and yarn size on yarn water transport rates, previously described [5], would also be evident in the water transport rates of fabrics made from the yarns.

**TABLE II. A Comparison of Water Movement in Yarns and Fabrics**

| Sample no. | Fabric description | Distance water transport rate $k_s$ | |
|---|---|---|---|
| | | Fabric (cm.²/sec.) | 2-Ply yarn (cm.²/sec.) |
| 48 | 100% Cotton serge | 0.16 | 0.45 |
| 68 | 100% Cotton underwear | 0.20 | 0.34 |
| $N_2$ | 100% Nylon serge | 0.18 | 0.23 |
| 743 | 70/30 Wool/Orlon serge | 0.057 | 0.089 |
| 70* | 100% Wool underwear | 0.029 | 0.052 |
| 742 | 70/30 Wool/Dacron serge | 0.038 | 0.046 |
| 26 | 70/30 Wool/Orlon serge | 0.0049 | 0.0004 |
| A | 100% Wool serge | 0.0031 | 0.0012 |

* Sample treated to make it wettable.

It is interesting to note that in this data, as in that of Table I, the wool-rich blends tended to have lower water transport rates than the fabrics of all synthetic or cotton fiber content. This too reflects the type of behavior observed in individual yarns [5] and suggests that the random arrangement of the wool fibers in these yarns is directly responsible for the low fabric-wicking rates observed. The consequences of changing fiber arrangement without changing fiber content of the fabrics are considered in a subsequent section.

## Water-Holding Capacity and Water Movement in Fabrics

It is important to distinguish between the rate at which water moves along a fabric in terms of the distance traveled and the amount of water transported over a given distance in unit time. The latter is called the "mass" water transport rate $k_m$ and has been defined in Equation 3. It was assumed that the two rates would be related simply, as in Equation 2, in terms of the amount of water a fabric could hold on being wet, called its water-holding capacity.

The water-holding capacity $m_w$ of a number of the experimental fabrics and their "distance" water transport rates were determined, as has been described. From these figures, values of the "mass" water transport rate were calculated using Equation 2. At the same time mass water transport values were determined experimentally using the manometer data from the horizontal fabric strip method, along with Equation 3. Values of the constants $k_m$ obtained in both ways for 17 fabrics are compared in Figure 3. The log-log plot was used only for convenience in encompassing the wide range of rate values obtained with these fabrics. The agreement between the theoretical correlation slope of unity and the water transport data is excellent over a thousandfold change in rate and over a sevenfold range of water-holding capacity. From the meaning of the rate constant, $k_m$ (Equation 3), it is easily seen that

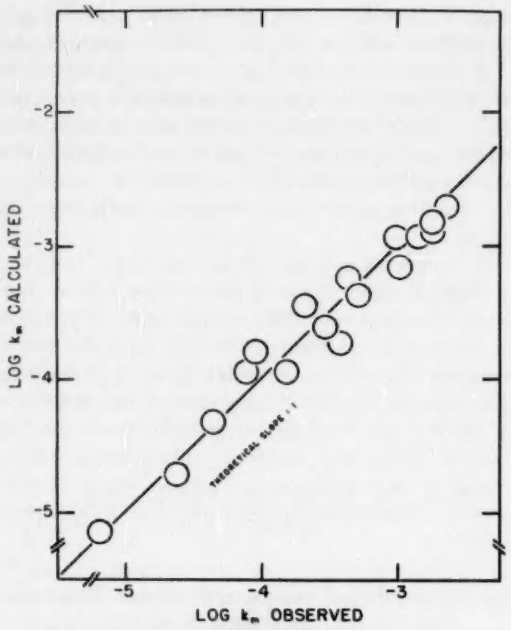


FIGURE 3. "MASS" WATER TRANSPORT RATES, $k_m$, FOR SEVERAL FABRIC TYPES

the large differences in the amount of water carried by different fabrics, starting from the dry state, results mainly from differences in the basic structure of these materials. These structure differences can be interpreted, then, as differences in the size and continuity of capillary spaces $r_e$ and as variations in the arrangement of the individual fibers of the yarns as they affect the yarn roughness factor cos $\theta_A'$.

### Water Transport and Fabric Properties

From the various series of blended serge fabrics which formed a major part of these studies, four wool/Orlon fabrics were selected which exhibited some rather interesting properties. These fabrics, made to conform to Army specification serges (MIL-C-823A), were indeed similar in thickness, weight, and texture and contained yarns of comparable size, twist, crimp, and fiber count. However, they differed appreciably in their ability to transport water, as indicated by their transport rates and surface wetting times, given in Table III.

Yarns were taken from these fabrics and their water transport rates determined. These values, along with contact angles of water on the yarns, are also given in Table III. From the contact angles, cosines were calculated, and the substitution of these values in Equation 1 would account, in general, for the nature of the differences in water transport rates observed in both yarns and corresponding fabrics. As these types of variation in contact angle have been shown to depend almost entirely on yarn structure [5], it was concluded that these fabrics differed mainly in the way in which the fibers were arranged in the yarns. As was observed in the microscopic field of the contact angle apparatus, the fibers in the yarns of fabric 26 were very randomly arranged, and the contact angle remained high. On the other hand, the fibers in the yarns of sample 741 appeared to be aligned to the highest degree of the group studied, with a correspondingly lower contact angle. The lower contact angles were accordingly associated with faster water movement in both the yarns and fabrics of the blended samples of this study. Thus, in this series of blended fabrics, water transport or "wicking" properties could not be predicted from the types of fibers used in the blend. Indeed, these particular results indicated that within limits, the wettability of blends could probably be controlled by altering the type of fiber arrangement in the yarns of the fabrics.

The specific thermal resistances of three of these materials containing added moisture were also determined, and these values are included in Table III. The samples with established random fiber arrangement in the yarns gave the greatest insulation in these experiments. This result is in agreement with con-

**TABLE III. The Relation of Water Transport Rates to Other Properties of Several Wool/Orlon Serge Fabrics ***

| Sample no. | 26 | 8 | 743 | 741 |
|---|---|---|---|---|
| Fabric water transport rate $k_s$ (cm.²/sec.) | 0.005 | 0.033 | 0.043 | 0.057 |
| Surface wetting time $t_s$ (sec.) | 2740 | 200 | 160 | 155 |
| Yarn water transport rate $k_s$ (cm.²/sec.) | <0.001 | — | 0.025 | 0.047 |
| Yarn advancing contact angle $\theta'_A$ (degrees) | 119 | 72 | 59 | 57 |
| Cosine yarn contact angle cos $\theta'_A$ | <0.001 | 0.31 | 0.52 | 0.55 |
| Specific thermal resistance, wet fabric† $\left(\frac{m^2 \text{ sec. C}^\circ}{\text{cal. in.}}\right)$ | 1.65 | — | 1.45 | 1.38 |

* All fabrics 70% wool, 30% Orlon, except sample 8 containing 65% wool, 35% Orlon.

† Thermal resistance measurements made using the Cenco Fitch apparatus on fabrics containing 50% by weight of added moisture.

clusions from a similar study on blended fabrics in which fiber arrangement was varied by changing the blend composition [1]. Thus, for these blended wool/Orlon fabrics, fiber arrangement, water transport behavior, and thermal conductivity appeared to be interdependent fabric properties. This conclusion suggests that the randomness of fiber arrangement in blended yarns may be an important factor to consider in the preparation of fabrics with suitable thermal properties for clothing use. Blended fabrics which were prepared with this idea in mind are currently being studied.

## Conclusions and Discussion

Comparative studies of the rate of movement of water along fabrics have shown that the penetration of the capillaries formed by the fibers in the yarns accounts for most aspects of water transport behavior. Both the amount of water carried by the fabric and the distance that it travels in unit time are influenced considerably by the randomness of the arrangement of the fibers in the yarns. The same factor seems to control the ease of wetting of the surface of the fabrics. It should be pointed out, however, that this behavior is not necessarily indicative of how the same fabric would behave under a hydrostatic head of water, as from the impact of rain drops [8]. Indeed, rain penetration of a fabric depends also on interyarn pore size, and pore size distribution [7].

The large differences in water transport properties exhibited by fabrics can be used as a sensitive index of the type of fiber arrangement in their yarns. Since the drop absorption technique seems to relate well to the actual water transport rates observed in fabrics, it may be used as a simple means for assessing fiber arrangement in the yarns of fabrics. For blended wool-type fabrics at least, the randomness of fiber arrangement in yarns is related to a number of other properties. For example, wool-rich blends tend to be thicker and to provide better insulation than those high in synthetic fiber content because of the less orderly arrangement of the wool fibers in the yarns. This, of course, is a consequence of the high degree of crimp and natural variation of diameter and length found in these fibers.

In the preparation of blends in which the fiber arrangement has been altered to change these yarn and fabric properties, the drop absorption method can be used as a guide in evaluating the effectiveness of this alteration. In order to form a detailed picture of the yarn structure, the measurement of yarn and fabric horizontal water transport rates, as well as yarn contact angles, could also be recommended.

## Acknowledgment

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# Microscopical Observations on Partially Acetylated Cottons and Related Fibers[1]

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**Abstract**

Effects of acetylation on the morphology and submicroscopic structure of cotton have been studied by light and electron microscopy. The cross-sectional area of partially acetylated (PA) fibers increases with degree of substitution. The average refractive index of PA cotton decreases with increase in acetyl content, as do the indices measured parallel and perpendicular to the fiber axis. Refractive index measurement appears to be a feasible method for estimating the chemical composition of PA cotton. At early stages of esterification, unevenness of reaction along the length of fibers may be demonstrated by dyeing and swelling techniques.

Acetylation causes the surface of cotton to become smoother, and obliterates the microfibrillate pattern characteristic of scoured fibers. PA cotton fibers swell when embedded in methacrylic esters by polymerization. The swelling causes separation of the lamellae of the secondary wall, and permits electron microscopical observations on the interior elements of the fiber to be made on thin cross sections of the specimen.

Fragments of PA cotton obtained by wet-beating show progressive loss of the fibrillate character of unacetylated cellulose as the acetyl content increases. At high degrees of substitution, the PA cotton fragments resemble the spongy particles obtained from wet-beaten acetate rayon and Arnel.

The results of microscopical examination are considered in terms of fiber structure.

WHILE many of the phenomena associated with chemical modification of cotton and other cellulosic fibers take place at the amicroscopic level, the effects of the modification are apparent in even cursory microscopical examination. From a mechanistic viewpoint, the interrelationships of each of the morphological domains of a system are continuous. In a cellulose fiber, changes at the molecular level are reflected in its fine-structural units and ultimately in its total morphology. Visualization of these changes is perhaps the most important contribution that microscopy can make in attacking the physical problems of fiber research. From such observations, new methods applicable to both research and quality control are frequently evolved.

A survey of the microscopical and submicroscopical aspects of a number of chemically modified cottons has been undertaken at this laboratory. Since other properties of partially acetylated (PA) cotton have been studied here and elsewhere for a number of years, special attention was devoted to this modification. Apart from being representative of an important mode of reaction of cellulose, PA cotton may be regarded as an example of the creation of a textile product to meet specific end uses. Its resistance to heat and microbial attack, for example, is considerably superior to that of unmodified cotton and of many other cellulose derivatives. Since the cotton retains its fibrous form, the inherent advantages of unmodified cotton are also present in the esterified product. Commercial production on a limited scale has been undertaken.

The light microscope was used to study the relationship of the acetyl content of PA cotton fibers to their average cross-sectional area, refractive indices, and response to swelling agents and dyes. Surface replicas, cross sections and fragments of PA cotton were examined in the electron microscope. Some of the observations were extended to include samples of commercial acetate rayon and cellulose triacetate (Arnel).

[1] Presented at the Spring Meeting of the Fiber Society, Clemson, S. C., May 2–3, 1956.

[2] Present address: General Electric Corp., Louisville, Ky.

[3] One of the Laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U.S. Department of Agriculture.

The PA cottons varied in acetyl content from approximately 5% to approximately 45% (cellulose triacetate). All were in the fibrous form. The original samples differed to some extent in form and method of preparation. All were prepared and analyzed by the Cotton Chemical Processing Section of this laboratory. The cottons having 5 to 27% acetyl content were acetylated in fabric form, using a mixture of acetic anhydride and acetic acid ($HClO_4$ catalyst) (Method A) [4, 2]. One sample (34% acetyl) was also esterified by this technique, but was reacted in the form of loose fiber. Samples of higher acetyl content were prepared from loose fiber, employing a mixture of acetic anhydride and amyl acetate ($HClO_4$ catalyst) (Method B) [2]. The conditions pertaining to each sample are listed in Table I.

## Light Microscopical Observations

### *Cross-Sectional Area Measurements*

Fiber sections were prepared by means of the Hardy hand microtome.[4] The nitrocellulose lacquer which is a satisfactory embedding medium for many fiber types was found to cause distortion of the cross-sectional shape of some PA cottons. It was abandoned in favor of a water dispersion of polyvinyl alcohol [3]. Fibers removed from fabric yarns and other samples were parallelized before being placed in the slot of the Hardy device. It was found that section-cutting could be done with increased facility if the cotton fibers were interspersed with nylon filaments in the slot. Fiber sections were mounted in heptane and photographed at a magnification of 500×. After enlargement to 1000×, the areas of 200 fibers of each sample were measured with a polar planimeter. In order to eliminate subjective discrimination, every effort was made to measure all fiber cross sections in each photograph. The standard error of the average areas was 3–4% for each sample measured. The results of the measurements are given in Table I.

The measurements show that, in general, an increase in degree of substitution is accompanied by an increase in cross-sectional area. In the range of acetyl content 17–22%, at which the PA cotton shows good resistance to heat and cellulolytic activity, the fibers were 25–30% larger than the unacetylated cotton. At high substitutions, the fiber cross section has approximately doubled that of the control. The relatively large cross-sectional area of the 34% acetyl sample was probably brought about by the swelling which occurs during acetylation in the presence of large amounts of acetic acid; such swelling becomes marked when the acetyl content of the fibers reaches 30% [2].

A comparison of the volume changes and cross-sectional area changes of the cottons as a result of acetylation should indicate whether the fibers have undergone axial shrinkage or expansion. If volume increases are equal to area increases, it is obvious that no change in fiber length occurred. Volume changes may be estimated from the densities of the PA cottons. The gradient column method was used to measure densities [6, 12]. Values obtained for the PA cottons measured are listed in Table I, along

[4] It is not the policy of the Department of Agriculture to endorse the products of one manufacturer over similar products of other manufacturers.

**TABLE I. Cross-Sectional Areas of Unacetylated and Partially Acetylated Cotton Fibers**

| Acetyl content, % | Degree of substitution | Form | Method of preparation | Cross-sectional area, $\mu^2$ | Increase in area, % | Density,* g./cc. | Volume increase,† % |
|---|---|---|---|---|---|---|---|
| 0 | 0 | Fabric | — | 135 | — | 1.550 | — |
| 5 | 0.20 | Fabric | A | 154 | 14 | 1.533 | 6 |
| 8 | 0.32 | Fabric | A | 148 | 10 | 1.519 | 11 |
| 14 | 0.61 | Fabric | A | 162 | 20 | 1.490 | 21 |
| 17 | 0.76 | Fabric | A | 169 | 25 | 1.464 | 27 |
| 22 | 1.09 | Fabric | A | 175 | 30 | 1.435 | 39 |
| 27 | 1.42 | Fabric | A | 205 | 52 | 1.407 | 52 |
| 0 | 0 | Fiber | — | 133 | — | 1.550 | — |
| 34 | 1.92 | Fiber | A | 255 | 92 | 1.394 | 68 |
| 41 | 2.58 | Fiber | B | 244 | 83 | 1.356 | 93 |
| 45 | 3.00 | Fiber | B | 271 | 104 | 1.332 | 106 |

* Measured by density gradient method [6, 12].
† Calculated from density and weight increase.

with the volume changes with respect to the control cottons.

Most of the PA cottons showed volume increases approximately equal to their increases in cross-sectional area. An exception was noted in the 34% acetyl sample, where the increase in area was considerably greater than the volume increase, indicating that axial shrinkage of the fiber accompanied lateral expansion. The good agreement of the volume and area increases is evidence for the predominantly lateral orientation of the acetyl group with respect to the fiber axis. Since addition of acetyl groups does not change the length of the fiber, as judged by most of the samples examined, it is probable that the over-all orientation of the cellulose chains in the fiber is not affected to a great extent as a result of acetylation.

*Refractive Index Measurements*

The changes in refractive index that accompany modification of the chemical nature, crystal lattice, or orientation of cellulose and its derivatives have received considerable attention in the past. Such observations have been made the basis of fiber identification, and have been used to evaluate orientation of the cellulose chains. Refractive indices of PA cotton have not, as yet, appeared in the available literature. The extension of such a technique to PA cotton appears to be entirely feasible, and seems to deserve consideration as an analytical tool for such materials.

The immersion method of refractive index measurement is usually employed in the study of fibers. The direction of shift of the Becke line when the microscope is defocussed slightly indicates the refractive index relationship of the fiber and the medium in which it is immersed [8]. Shillaber oils [4] were used in the measurements reported in this paper. No interaction or swelling of the fibers was noted when they were placed in contact with the oils. White light was employed for the observations. In determining the refractive indices with respect to light vibrating parallel to and perpendicular to the fiber axis, a cap analyzer was used [8]. Measurements were made at room temperature (25°–26° C.), and are precise to 0.001. When the indices of fiber and oil matched, the specimen was allowed to remain in contact with the oil overnight, after which deviations from matching were sought. In no case was any change occurring during this period observable. The index for each sample did not vary from fiber to fiber in that sample, except in the PA cottons of the lowest and highest ranges of acetyl content. The refractive index value for each sample was checked on 12 fibers from that sample. The results of the measurements are listed in Table II, which also includes data for acetate rayon (filament), Arnel (staple), and saponified cotton cellulose triacetate.

The average refractive index of cotton (measured in unpolarized light) shows a continuous decrease as the acetyl content increases. The same is true for the indices measured with light vibrating parallel ($n_{\parallel}$) and perpendicular ($n_{\perp}$) to the fiber axis. Within the error of measurement, the average refractive index for each specimen was the arithmetic

**TABLE II. Refractive Indices of Partially Acetylated Cottons and Related Fibers**

| Acetyl content, % | Method of preparation | Average refractive index | $n_{\parallel}$ | $n_{\perp}$ | Birefringence $n_{\parallel} - n_{\perp}$ |
|---|---|---|---|---|---|
| 0 | — | 1.555 | 1.578 | 1.532 | 0.046 |
| 5 | A | 1.549 | 1.572 | 1.526 | 0.046 |
| 8 | A | 1.544 | 1.565 | 1.522 | 0.043 |
| 14 | A | 1.532 | 1.551 | 1.513 | 0.038 |
| 17 | A | 1.528 | 1.545 | 1.512 | 0.033 |
| 22 | A | 1.516 | 1.529 | 1.504 | 0.025 |
| 27 | A | 1.506 | 1.514 | 1.498 | 0.016 |
| 34 | A | 1.495 | 1.499 | 1.492 | 0.007 |
| 41 | B | 1.487 | 1.490 | 1.484 | 0.006 |
| 43 | B | 1.479 | 1.480 | 1.478 | 0.002 |
| 45 | B | 1.471 | 1.470 | 1.472 | −0.002 |
| Acetate rayon (38%) | — | 1.476 | 1.478 | 1.474 | 0.004 |
| Arnel (45%) | — | 1.472 | 1.472 | 1.472 | 0.000 |
| Saponified acetylated cotton (0% Acetyl) | — | 1.550 | 1.570 | 1.530 | 0.040 |

mean of $n_{\parallel}$ and $n_{\perp}$. A plot of the average refractive index $n$ as a function of acetyl content of the sample is shown in Figure 1, which also includes similar plots for $n_{\parallel}$ and $n_{\perp}$. The curve obtained, although roughly linear over a considerable range, does not appear to fit any simple mathematical expression. Considered as an empirical relation, however, it would appear to be useful in estimating the degree of substitution of acetylated cotton prepared under the conditions represented by these samples.

Figure 1 also shows that the rate of decrease with acetyl content of $n_{\parallel}$ is greater than that of $n_{\perp}$. At higher acetyl contents, these two indices approach each other and the fiber becomes virtually optically isotropic. The decrease in birefringence $(n_{\parallel} - n_{\perp})$ actually proceeds until a negative value is obtained in the region of 44–45% acetyl. Acetate rayon, containing approximately 38% acetyl, has refractive indices somewhat lower than PA cotton of similar chemical composition. The values for Arnel are substantially the same as those of cotton in the fully acetylated state. The birefringence of Arnel, although zero as measured by the immersion method, appears to be slightly negative when the fibers are observed between crossed polarizers and a selenite retardation plate [8].

The immersion method of measuring refractive index provides a value which is characteristic only for the periphery of the fiber. The relation of the index measured in this way to that of the fiber interior can be judged by comparing the values of the molar refraction of cellulose acetate obtained from the observed data with those calculated by addition of the atomic and group refractions in the molecule. The calculated and observed molar refractions of the PA cottons are listed in Table III. Incremental molar refractions for the $CH_2$, C, H, and hydroxyl, ether, and carbonyl oxygen groups were taken from published tables based on the Lorentz-Lorenz formula [1]. The observed molar refraction $R$ was obtained by substitution in the Lorentz-Lorenz equation

$$R = \frac{(n^2 - 1)\,M}{(n^2 + 2)\,d}$$

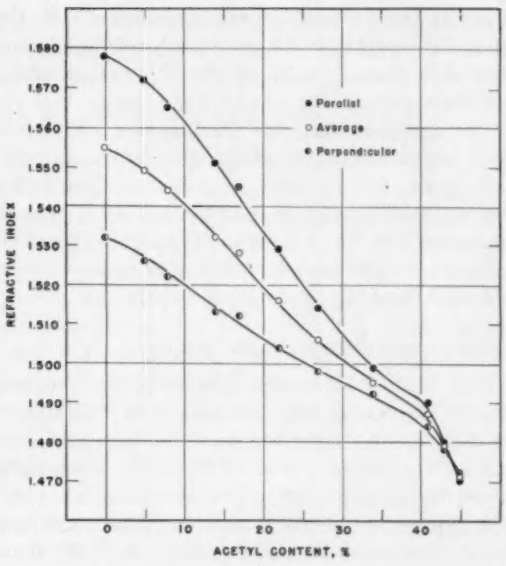



**Fig. 1.** Relation of acetyl content to refractive indices of PA cotton measured in unpolarized light ($n$) and with light vibrating parallel to ($n_{\parallel}$) and perpendicular to ($n_{\perp}$) fiber axis.

**TABLE III. Calculated and Observed Molar Refractions of Partially Acetylated Cottons**

| Acetyl content, % | Average molecular weight of acetylated glucose unit | Refractive index, $n$ | Density, g./cc. | Molar refraction | |
|---|---|---|---|---|---|
| | | | | Calculated | Observed |
| 0 | 162 | 1.555 | 1.550 | 33.4 | 33.5 |
| 5 | 170 | 1.549 | 1.533 | 35.2 | 35.3 |
| 8 | 175 | 1.544 | 1.519 | 36.4 | 36.4 |
| 14 | 188 | 1.532 | 1.490 | 39.0 | 39.1 |
| 17 | 194 | 1.528 | 1.464 | 40.4 | 40.8 |
| 22 | 208 | 1.516 | 1.435 | 43.4 | 43.8 |
| 27 | 222 | 1.506 | 1.407 | 46.5 | 46.9 |
| 34 | 239 | 1.495 | 1.394 | 51.1 | 50.0 |
| 41 | 270 | 1.487 | 1.356 | 57.4 | 57.3 |
| 43 | 279 | 1.479 | 1.340 | 59.2 | 59.0 |
| 45 | 288 | 1.471 | 1.332 | 61.1 | 60.4 |

where $n$ is the average refractive index, $M$ the molecular weight of the acetylated anhydroglucose unit, and $d$ the density of the PA cotton under consideration.

The agreement between the observed and calculated molar refractions of the PA cottons is relatively good, and indicates that the refractive index measured at the edge of the fiber is close to that of the material within the fiber. The use of refractive index to estimate acetyl content thus appears to be valid for the PA cottons in this study.

*Response to Swelling Agents and Dyes*

Esterification of cotton even to a small extent changes the rate of response to such swelling agents for cellulose as cuprammonium or cupriethylenediamine hydroxide. When PA cotton fibers were placed in contact with cupriethylenediamine solution adjusted to produce slow but steady swelling and dissolution of untreated cotton (*ca.* 0.25 *M* in Cu), the effect on the fiber during the ensuing 10 min. varied with the acetyl content. Microscopical observations showed that the fibers of 5% acetyl content swelled and dissolved at a significantly slower rate than unacetylated cotton. At the 8% acetyl level, extremely uneven swelling was noted; some portions of the fiber swelled only slightly. In fibers containing 14% acetyl, little or no swelling was observed, and all samples of higher acetyl content were virtually unaffected during the period of observation. Eventually, of course, saponification of the ester groups permitted dissolution of the cellulose of all of the samples.

Acetone had relatively little effect on any of the PA cottons, although there was slight swelling in the fibers in the intermediate degrees of substitution (17–34% acetyl). This effect was also noted in fibers of this range of substitution when they were placed in contact with nitrocellulose lacquers containing lower ketones and esters. PA cottons up to 34% acetyl content showed no swelling in *s*-tetrachloroethane. Those of higher degrees of substitution showed various degrees of swelling and dissolution when placed in this solvent.

When PA cottons are dyed in a bath containing both direct and acetate dyes, the resulting color is an index of the extent and evenness of esterification [4]. In this study, the cottons were dyed in a mixture of Pontamine Fast Heliotrope B[4] (C.I. Pr. 367) and Celliton Fast Yellow RRA[4] (C.I. Pr. 243) in water solution containing a dispersing agent, according to the procedure of Goldthwait [4]. The color of the fibers in samples containing 14% or more acetyl was almost or completely yellow in every case. At the 5% acetyl level, the fibers were predominantly the color of the heliotrope direct dye, although regions of yellow were present, and a few completely yellow fibers were seen. In the 8% acetyl sample, both heliotrope and yellow fibers were present in approximately equal numbers, and examination of individual fibers showed that both colors frequently existed in the same fiber. The colors in these fibers alternated in bands along the length of the fiber, a yellow band succeeding a purple one, with little or no admixture of the colors in any band.

When the fibers showing uneven coloring were observed between cross polarizers, the alternation in color was seen to be related to the position of the spiral reversals in the fibers. This phenomenon is illustrated in Figure 2. The alternation of light (yellow) and dark (heliotrope) regions is evident in unpolarized light. When the identical fiber area is examined between crossed polarizers, with the fiber axis parallel to the plane of the polarized light, the narrow dark bands showing the location of spiral reversals are seen to be in the yellow regions. In most fibers the extinction band was located well within the yellow regions, as shown in Figure 2. Frequently the reversal point was near the junction of a direct-dyed and yellow region but seldom, if ever, in a direct-dyed band.

The variation in acetyl content along the length of the fiber that was shown up by the dye test could

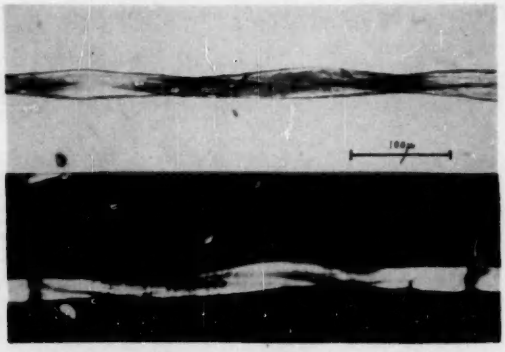


**Fig. 2.** Photomicrographs of PA cotton fiber (8% acetyl content) dyed with yellow acetate (light regions) and heliotrope direct (dark region) dyes. Above: unpolarized light. Below: polarized light; fiber axis parallel to plane of polarizer.

also be demonstrated by corresponding differences in refractive index. Similarly, the response of such fibers to cupriethylenediamine swelling differentiates the regions of lower and higher acetyl content.

These observations indicate that acetylation may initiate or proceed at a more rapid rate in the vicinity of spiral reversals in cotton fibers. Heuser, in discussing the role of fiber morphology in controlling reaction rate during acetylation [7], mentions the heterogeneity of reaction of ramie fibers acetylated in an acetic anhydride-benzene mixture. Under non-swelling conditions, acetylation proceeded to high substitution in some regions of the fiber, but areas between these regions remained unacetylated. The PA cottons of the present study were prepared under conditions which produce limited fiber swelling. If the direction of the cellulose chains at spiral reversal points is more nearly parallel to the fiber axis, greater transverse swelling of the fiber at these points would be expected to occur. On the other hand, the region of spiral reversals is regarded as containing cellulose fibrils under uneven stress distribution; swelling should cause rupture of some cellulose chains and permit increased accessibility of the cellulose to reagents. As acetylation proceeds, swelling of the acetylated region by the reagent medium would continuously open new areas for reaction.

## Electron Microscopical Observations

### *Surface Aspects of PA Cotton*

The change in topography which occurs when cotton fibers are acetylated was studied by means of surface replicas. The "two-stage" process was employed to reproduce the fiber surface [5]. In this method, an initial impression is taken in plasticized polystyrene film and coated with carbon by vacuum evaporation. The polystyrene is carefully dissolved away, and the carbon replica remaining is "shadowed" to emphasize surface irregularities. In Figure 3, the surface of a scoured fiber is compared with that of a fiber acetylated (25% acetyl content) after scouring. Two differences may be noted. The microfibrillate pattern of the surface of the scoured fiber does not appear in the acetylated fiber. While no fibrillate matrix is visible in unscoured cotton surfaces, it is readily demonstrated after kier-boiling procedures [9]. In none of the surfaces of the PA cottons examined was there any indication of a microfibril system. Acetylation presumably causes swelling and disruption of the cellulose elements at this point in the fiber. A second difference between unacetylated and acetylated fibers is in the over-all smoothness of the surface. Fewer ridges and valleys are noted in acetylated fiber surfaces. In view of the increase in cross-sectional area that occurs, this smoothing-out effect is to be expected.

### *Cross-Sectional Appearance of PA Cottons and Other Fibers*

The techniques for obtaining extremely thin sections of fibers and other organic materials have been described elsewhere [10, 11, 14]. Considerable difficulty was experienced in producing such cross sections of cotton and most of the other fibers included in this study. It was found that the most satisfactory embedding medium was a 4:1 mixture of methyl and butyl methacrylates. Polymerization of the mixture to sufficient hardness was accomplished by heating at 55° C. for 16 hr., using 0.5% 2,4-dichlorobenzoyl peroxide as catalyst. Sections of the embedded fibers were floated from the knife edge on the surface of a 1:1 dioxane-water mixture.

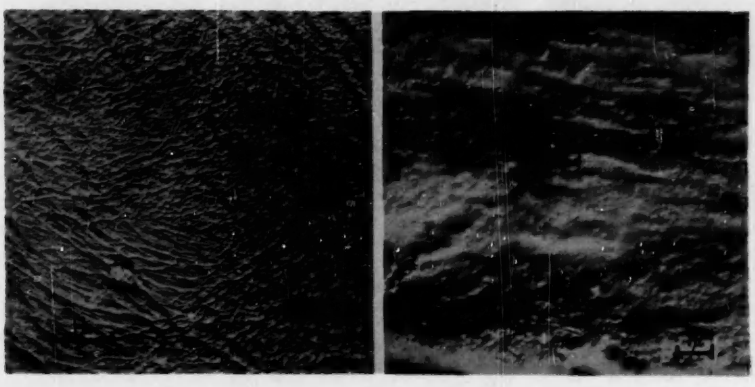


**Fig. 3.** Electron micrographs of surface replicas of unacetylated scoured cotton fiber (left) and of fiber acetylated after scouring (right).

They were removed from the liquid surface with a small platinum loop and placed on specimen grids covered with a silicon monoxide supporting film. The polymethacrylate was removed by allowing the grids to rest overnight on a piece of filter paper saturated with toluene. In most cases the polymethacrylate was removed completely by this procedure, but some embeddings showed the presence of a material which did not yield to a wide variety of organic solvents. The fiber sections were shadowed prior to examination in the electron microscope.

Figure 4 is an electron micrograph of a cross section of an untreated cotton fiber. In nearly every section prepared, mechanical damage and distortion of the original arrangement of the specimen were obviously present, but the over-all architectural details of the fiber were retained. Relatively little detail of the structure of the interior of the fiber can be seen, although there is some evidence for the existence of a lamellate arrangement in the cell wall. The occurrence of microfibrils at the outer and inner edges of the cell wall is unmistakable, as is their highly parallel arrangement.

PA cotton fibers embedded in bulk-polymerized methacrylic esters underwent swelling of the cell wall [14]. The swelling was accompanied by separation of the wall into concentric layers. Observations of the progress of swelling in fibers under the microscope showed that it occurred during the early stages of polymerization. Swelling was also noted in fibers embedded by polymerization of styrene, but in this case, over-all expansion of the cell wall, without separation into layers, took place. Other embedding media (paraffin, polyethylene glycol), while causing no swelling, were found unsuitable for the production of sufficiently thin cross sections.

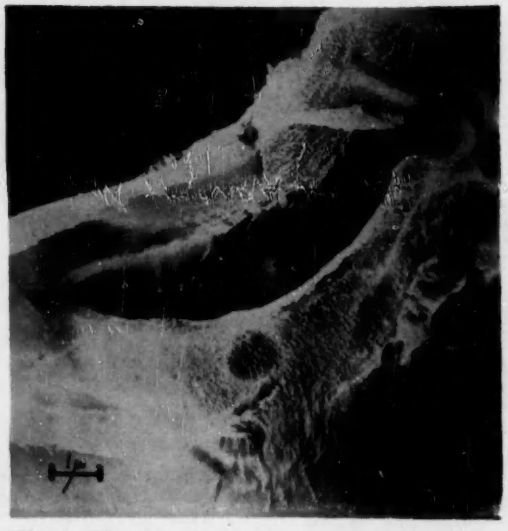


**Fig. 4.** Electron micrograph of a cross section of an untreated cotton fiber. Palladium shadowing.

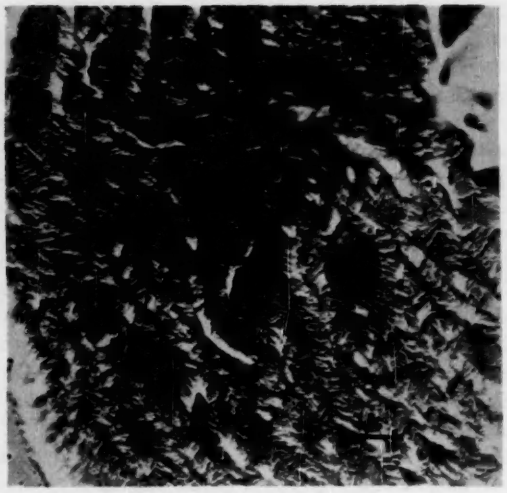


**Fig. 5.** Electron micrograph of a cross section of a PA cotton fiber (25% acetyl content). Palladium shadowing.

The typical appearance of sections of PA cotton in the electron microscope is shown in Figure 5. The specimen in this micrograph was cut from a sample containing 25% acetyl. The swelling that accompanied polymerization of the embedding medium has increased the distance between the lumen and the periphery of the fiber from about 4 $\mu$ to approximately 20 $\mu$. The microfibrils which make up the secondary thickening of the fiber are well-defined. The fibrils are arranged in layers roughly concentric to the main axis of the fiber. There is considerable separation of the layers along the radius of the fiber section, but relatively good cohesion of the fibrils in any single layer. In many cases the width of the microfibrils is less than 100 A.

Most of the specimens prepared were free from material with a swollen or gel-like appearance. However, some cross sections possessed a typical gel structure, in which discrete microfibrils were obscured by obviously swollen material. The presence or absence of gel structure did not seem to be associated with the type of solvent used to remove the polymethacrylate embedding.

A cross section typical of those obtained from a sample of PA cotton containing 15% acetyl is shown in Figure 6. Swelling and separation of layers are evident at the outer region of the cell wall, but a core of unswollen material remains in the inner region. The appearance of the unswollen portion is similar to that of unacetylated cotton (Figure 4), indicating that the fibers of this sample were unevenly reacted. Cross sections of fully acetylated cotton were similar in appearance to those acetylated to 25% acetyl content.

The appearance of a cross section of an acetate rayon filament is shown in Figure 7. The characteristic lobes of the periphery of the filament are clearly seen. Although little structure can be discerned in the interior of the filament, the edge shows oriented fibrils. Peck and Kaye [13] have shown that these fibrils are more easily seen in stretched filaments than in unstretched. In contrast to the behavior generally observed for PA cottons, no swelling or disruption of the acetate rayon on embedding in methacrylate was noted.

The separation of the cell wall of PA cotton into concentric layers is undoubtedly a reflection of the natural structure of the fiber. Since such a phenomenon does not occur in unacetylated cotton under normal conditions, the pattern of swelling is related to the location of esterified regions in the fiber. The discontinuities observed when cross sections of cotton are swelled in cuprammonium hydroxide may be correlated with alternations in the rate of cellulose deposition during thickening of the cell wall. The similar pattern appearing in embedded PA cotton points to alternations in the radial distribution of acetyl groups. The swelling is the result of the formation of osmotic cells within the fiber, since methacrylates undergo shrinkage on polymerization and would not in themselves cause expansion of the fiber. If it is assumed that the esterified regions of the fiber permit increased diffusion of the methacrylate, then polymerization of the monomer would set up osmotic forces across an unesterified cellulose barrier. Since a similar result does not occur in acetate rayon filaments, it is apparent that no osmotic forces were operative during the polymerization of methacrylate in this material. The distribution of acetyl groups in acetate rayon is completely uniform, and no unesterified regions exist to serve as osmotic cell membranes.

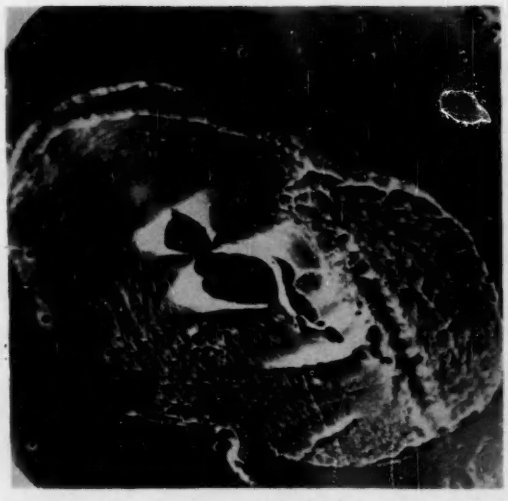


**Fig. 6.** Electron micrograph of a cross section of PA cotton fiber from sample containing 15% acetyl. Palladium shadowing.

**Fig. 7.** Electron micrograph of a cross section of acetate rayon filament. Palladium shadowing.

*Fibrillate Character of PA Cottons and Other Fibers*

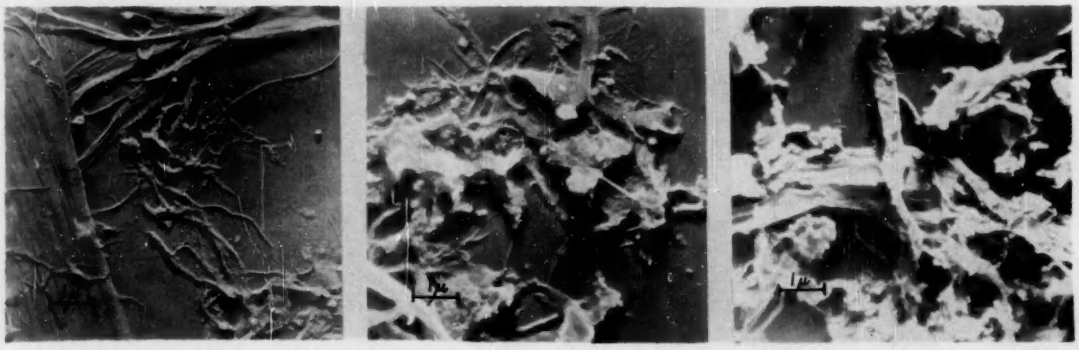
Reduction in the size of fiber components to thicknesses suitable for electron microscopy can also be accomplished by mechanical beating in water. In native cellulose, beating causes disruption of the fiber along natural cleavage lines. For cotton and similar fibers, cleavage occurs between successive growth layers and between microfibrils making up the growth

**Fig. 8.** Electron micrograph of fragments of cotton produced by beating untreated fibers in water in a Waring blendor for 15 min. Chromium shadowing.

layers. Separation into sheets which are portions of growth layers occurs earlier in the beating process than does fibrillation. The cohesion of the fibrils in the layers of the secondary wall (Figure 5) is another aspect of this behavior. More extended periods of beating cause breakdown of the sheets into small groups or single microfibrils. The appearance of fragments of untreated cotton produced by beating fibers in water in a Waring blendor [4] for 15 min. is shown in Figure 8. The thin sheet consists of cellulose microfibrils arranged in a highly parallel fashion. Practically no material of a nonfibrillate character appears in the field. The microfibrils are at least several microns long, and some 100–200 A wide. They are thinner than they are wide, as judged by the length of the shadows they cast.

Comminution of PA cotton by wet-beating yields fragments which may be markedly different than those from unacetylated fibers. In the lower degrees of substitution, the fragments are essentially similar to those of cotton itself. In specimens whose acetyl content was 17% or higher, however, fewer sheets and well-defined fibrils were noted, and the number of fragments of a relatively amorphous or spongy character increased. In samples of 22–27% acetyl content, the quantity of fragments having fibrillate structure was about equal to that having a spongy appearance. At higher acetyl contents, the amorphous component predominated in all fields examined. The micrographs in Figure 9 show examples of typical fragments from PA cottons of increasing acetyl content. The reduction of PA cottons to fragments suitable for examination required longer beating periods than did unacetylated fibers. The decreased water sorption of the esterified cellulose is probably responsible for this increased difficulty of fibrillation.

The spongy appearance of acetylated cellulose fragments has been noted previously [15]. The loss of fibrillate character conceivably can be brought about by plastic flow during beating. The over-all temperature during the procedure used in these studies rose to approximately 50° C. Transient temperatures in localized regions of the specimen would have been much higher, and thermoplasticity would have permitted flow in those portions of the specimen susceptible to high temperature. Attempts to lower



9a 9b 9c

**Fig. 9.** Electron micrographs of fragments of wet-beaten PA cottons of (*a*) 17%, (*b*) 25%, and (*c*) 41% acetyl content. Uranium shadowing.

the prevailing temperature during beating were only partially successful, and the appearance of the fragments was not changed in such experiments. However, the character of fragments of saponified cotton cellulose triacetate was similar to that of unacetylated cotton; this was true whether the acetate was saponified prior to or after reduction to fragments. Hence, any disorganization caused by plastic flow does not appear to carry over into the saponified cellulose. On the other hand, if acetylation takes place as a combination of topochemical and permutoidal reactions, the lateral order existing in the original cellulose will gradually be diminished. Mechanical cleavage would no longer follow lines determined by the original structure of the cellulose, but proceed along lines produced by the location of acetyl groups in relatively random regions of the fiber.

Fragments of acetate rayon and Arnel produced by the same technique as the PA cottons in Figure 9 are shown in Figure 10. Both specimens possess relatively little fibrillate character, and resemble highly acetylated cotton fragments. The micrographs published by Work [15] indicate the same type of structure in similar materials. Work also showed that the cellulose regenerated from cellulose triacetate was more fibrillate when the triacetate fiber was stretched prior to saponification. Since the cellulose chains in cotton are well-oriented, and cannot undergo much relative motion during acetylation, it is reasonable to assume that saponification of acetylated cotton would permit reorganization of the cellulose into groups similar to those existing in unacetylated fiber. The refractive index of saponified cotton cellulose triacetate is approximately that of slack-mercerized cotton, indicating an essentially similar arrangement of the cellulose molecules in the fiber.

The disappearance of the microfibrillate texture of the surface of scoured cotton as a result of acetylation (Figure 3) undoubtedly occurs during esterification. The cellulose exposed to high concentrations of reagent will reach a degree of substitution sufficient to become sensitive to the solvent power of the reagent. Cellulose on the surface of the fiber is also subject to disruption by the swelling which occurs as a result of acetylation, and which exerts its maximum effect on the peripheral layer of the fiber. Consequently, no pattern resembling that of the original fiber surface will remain.

## Conclusions

The effects of partial esterification on the morphology and submicroscopic structure of cotton appear to be readily detectable by microscopical methods. Perhaps the most sensitive of the methods used is measurement of refractive index, a parameter which is continuous throughout the entire range of substitution, and which can be directly related to the chemical composition of PA cotton. The use of refractive index as a means for estimating the acetyl content of PA cotton in a relatively rapid manner seems entirely feasible.

The change of cross-sectional area of the fiber which accompanies acetylation is greater, on an absolute basis, than other changes which take place in the fiber as a whole. The increase in cross-sectional area appears to account for much, if not all, of the increase in volume of the acetylated fibers. The increased effective diameter of PA cotton should bring about corresponding changes in the bending modulus of the fibers.

The structural patterns observed in acetylated cottons by both light and electron microscopy are useful in helping to place concepts of fiber architecture on a more valid basis. The lamellate arrangement

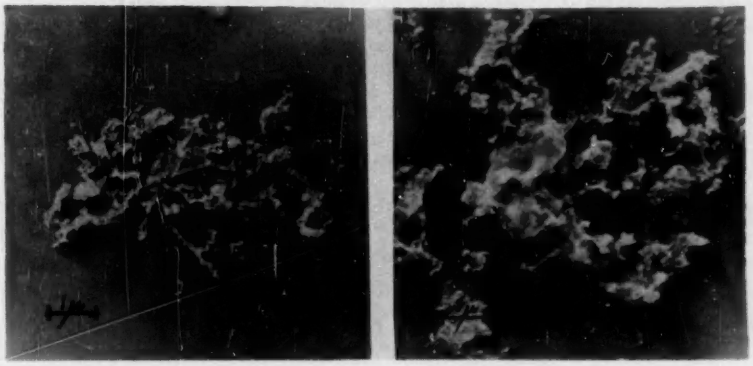


**Fig. 10.** Electron micrographs of fragments produced by wet-beating of acetate rayon (left) and Arnel (right). Uranium shadowing.

of secondary wall cellulose in native fibers is borne out convincingly by these observations. The influence of fiber morphology on rate and extent of reaction in acetylation has also been demonstrated, emphasizing the necessity for considering the chemical behavior of cellulosic fibers in terms of physical as well as chemical structures.

### Acknowledgment

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# The Influence of Micronaire Fineness and Prior Treatments on the Cyanoethylation of Cotton

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### Abstract

Fiber fineness, as measured by the Micronaire, and prior treatments have been found to be important factors in determining the rate and extent of cyanoethylation of cotton. Fineness was found to be a good index of the rate of reaction for both raw and pressure-boiled cotton fibers. Prior treatment of yarn by ethanol extraction, pressure boiling with 2% caustic, ethanolamine extraction, and mercerization—both slack and at constant length—affected the rate of cyanoethylation and the rot resistance of the product.

IN 1953, Compton and co-workers announced that important changes in the properties of cotton can be produced by partial cyanoethylation with acrylonitrile [2]. Since that time a number of studies have been reported by the Southern Utilization Research Branch, U.S. Department of Agriculture, dealing with the fundamentals of the reaction [4, 15], properties of the products [6, 9, 12, 13], and pilot plant methods of production [7].

[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U.S. Department of Agriculture.

The present paper reports a study of the cyanoethylation of cotton as influenced by the Micronaire [2] fineness and prior treatments. Interest in this investigation was aroused by findings in analogous studies of partial acetylation and other modification treatments where reaction rates and product differences were attributed to fiber properties of the cotton, or to treatments of the cotton by modification which might affect the fine structure. For example, Taylor and Owens [14] found that different varieties of cotton had different rates and degrees of acetylation. Grant, McDonald, and co-workers [5, 10, 11] have also shown that the properties of the product vary with differences in fiber properties. Daul, Reinhardt, and Reid [3] showed that the naturally occurring alkaline salts of grey cotton catalyzed the reaction of beta-propiolactone with cotton cellulose and that removal of these materials resulted in decreased reactivity.

Therefore, a number of prior treatments which affect cotton in different ways were investigated: namely, pressure boiling and ethanolamine extraction, both of which remove most of the noncellulosic constituents of cotton; ethanol extraction, which removes the waxes; and mercerization, both loose and at constant length, which affects the fine structure and accessibility of the cotton and removes some of its impurities.

Rot resistance of cyanoethylated cotton is believed to be due to blocking the hydroxyls of the accessible regions of cotton against microorganisms. Since prior treatments may have an effect on these accessible regions, a study of the rot resistance of cottons reacted equally, but differing in prior treatments, was included.

## Cottons, Prior Treatments, and Methods

### *Cottons*

The same six varieties of cotton raw stock used by Taylor and Owens in their acetylation study [14] were used. They were Acala 1517, Bobshaw, Empire, Lockett 140, Stoneville 2B, and an unknown variety grown in the Memphis area, which will be referred to in the text as "Memphis." In addition, two samples of Rowden, three samples of Deltapine, and one sample of Pima S-1 (irrigated) cottons were included in the study.

[2] Mention of names of firms or trade products does not imply endorsement or recommendation by the U.S. Department of Agriculture over other firms or similar products not mentioned.

A grey cotton 12/5 thread, such as is used for sewing bags, was selected for the study of the influence of prior treatments and of rot resistance.

### *Prior Treatments*

*a. Pressure boiling.* The fiber or yarn was boiled with 2% sodium hydroxide solution for 6 hr. under a pressure of 15 p.s.i., washed thoroughly with water, and air dried.

*b. Extraction with ethanolamine.* The test sample was extracted in a Soxhlet apparatus for about 6 hr. with ethanolamine, washed thoroughly with water, and air dried.

*c. Extraction with 95% ethanol.* The procedure was the same as for *b* except that the water washing was omitted.

*d. Mercerization.* Skeins of thread, either slack or held on a frame-type mercerizer at constant length were mercerized in 20% sodium hydroxide solution using Alkamerse R as wetting agent.[2] The mercerized thread was then washed with water, soured with dilute acetic acid, washed thoroughly with water, and air dried.

### *Cyanoethylation*

The fiber or yarn samples were cyanoethylated essentially as described by Daul, Reinhardt, and Reid [4]. The cotton was impregnated with 2% sodium hydroxide solution (containing Alkamerse R wetting agent), centrifuged to about 60% pickup, and treated with commercial grade acrylonitrile at 60 ± 1° C. for varying lengths of time. After the treatment, the samples were soured with dilute acetic acid, washed thoroughly with water, and air dried.

### *Test Methods*

Breaking strength (single strand method), fineness by the Micronaire method, and rot resistance were determined in accordance with the methods of the American Society for Testing Materials [1a, 1b, 1c, respectively]. The Micronaire finenesses obtained in this study are slightly higher for most of the cottons than those found by Taylor and Owens [14]. The pH of the rot test beds was 6.8 to 7.5. Nitrogen content was determined by the standard Kjeldahl method and calculated on a moisture-free basis.

## Experimental

### *Cyanoethylation of Raw Cotton Fiber*

Samples of the six varieties of cotton raw stock were cyanoethylated under comparable fixed condi-

**TABLE I. Cyanoethylation of Raw Cotton Fiber of Various Micronaire Fineness**

| Variety of cotton | Micronaire fineness | % N after reaction time, min. 15 | 30 | 60 | 120 |
|---|---|---|---|---|---|
| | Upland scale | | | | |
| Memphis | 2.53 | 4.4 | 6.0 | 9.1 | 10.1 |
| Empire | 3.78 | 2.9 | 4.5 | 6.5 | 10.5 |
| Stoneville 2B | 3.90 | 2.7 | 4.1 | 6.8 | 9.9 |
| Acala 1517 | 3.95 | 2.9 | 5.0 | 7.1 | 10.2 |
| Bobshaw | 5.00 | 2.4 | 3.8 | 6.3 | 9.6 |
| Lockett 140 | 5.68 | 2.1 | 3.4 | 4.6 | 8.9 |
| Spearman Rank Correlation Coefficients | $\rho_t$ = | −0.90 | −0.83 | −0.77 | −0.65 |

tions. The nitrogen content was taken as a measure of the degree of reaction. The resulting data for reaction times of 15, 30, 60, and 120 min. are given in Table I for the different cottons arranged in the order of increasing Micronaire indices. A definite relationship between nitrogen content and the fineness is readily apparent, the finer cottons (lower Micronaire indices) reacting more rapidly than the coarser cottons. To quantify this relation, the Spearman Rank Correlation Coefficient [3] was computed and found significant for each time of treatment, as shown in Table I. A somewhat lower correlation was obtained as the reaction time increased.

Although the Micronaire is ostensibly calibrated in units of fiber fineness, in reality it measures a function of the specific surface of the fiber. Thus, both intrinsic fineness and maturity are in effect measured jointly [8]. However, no attempt is made to evaluate separately the influence of fineness or maturity. The computations and conclusions are made from the Micronaire fineness alone.

The data in Table I suggest the possibility of predicting the time of reaction for a cotton of known fineness to obtain a specified nitrogen content. Accordingly, the values in Table I were interpolated for each of the cottons to give estimates of the reaction

[3] The Spearman Rank Correlation Coefficient $\rho$ was computed by the use of the formula

$$\rho = 1 - \frac{6 \Sigma d^2}{n(n^2 - 1)}$$

where $n$ is the number of pairs being compared and $d$ is the difference in rank between a pair of values. In event of ties, intermediate values are assigned, i.e., in the event of a tie for second and third place, both are assigned a rank value of 2½.

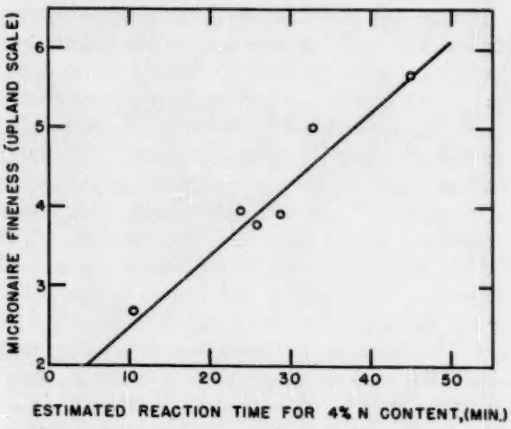


**Fig. 1.** Micronaire fineness versus estimated reaction time for 4% nitrogen content for raw fiber.

time required to obtain 4% nitrogen—the generally accepted threshold value for rot resistance [6]. The interpolated time values were plotted in Figure 1 against the Micronaire fineness and give an apparent straight-line relationship.

To verify this relationship, the six supplementary cottons, selected so as to provide a range of Micronaire values, were cyanoethylated for periods of time determined from their fineness and the regression line of Figure 1. The nitrogen contents of this series of cottons were all less than the 4% target value, the average being 3.3% (Table II). Thus there appears

**TABLE II. Cyanoethylation of Cotton Fibers for Times Based on Micronaire Fineness**

| Variety of cotton | Micronaire fineness | Time of treatment* $t$ min. | % N | % N/$t$ |
|---|---|---|---|---|
| | Upland scale | | | |
| Rowden | 5.98 | 50 | 3.63 | 0.0734 |
| Rowden | 4.85 | 34 | 3.25 | 0.0955 |
| Deltapine | 5.38 | 41 | 2.96 | 0.0730 |
| Deltapine | 4.32 | 29 | 3.55 | 0.122 |
| Deltapine | 3.78 | 23 | 3.35 | 0.145 |
| Pima S-1 | 4.00 | 26 | 3.17 | 0.122 |
| Avg. N content | | | 3.32 | |
| Spearman Rank Correlation Coefficient with Micronaire | | | 0.14 | −0.93 |

* Postulated from Figure 1.

**TABLE III. Cyanoethylation of Pressure-Boiled Cotton Fiber**

| Variety of cotton | Micronaire fineness | % N after reaction time, min. 15 | 30 | 60 | 120 |
|---|---|---|---|---|---|
| | Upland scale | | | | |
| Memphis | 2.58 | 4.0 | 5.6 | 9.2 | 12.0 |
| Empire | 3.78 | 2.7 | 4.2 | 6.3 | 10.4 |
| Stoneville 2B | 3.90 | 2.8 | 4.0 | 6.3 | 8.5 |
| Acala 1517 | 3.95 | 2.7 | 3.6 | 6.2 | 9.1 |
| Bobshaw | 5.00 | 2.1 | 3.0 | 4.6 | 6.7 |
| Lockett 140 | 5.68 | 2.0 | 3.0 | 4.5 | 7.1 |
| Spearman Rank Correlation Coefficient | $\rho_t$ = | −0.96 | −0.99 | −0.99 | −0.89 |

to be a difference in the level of reaction for this series. The Spearman Rank Correlation Coefficient between the Micronaire value and the nitrogen content was determined and found to be 0.14 (not significant), which is taken to be indicative that the Micronaire fineness–nitrogen content relationship may be eliminated by choosing times of treatment compensating for the difference in Micronaire fineness. If the effect of time is largely eliminated by use of the $\%N/t$ ratio, a highly significant correlation of −0.93 is observed between the Micronaire fineness and this ratio.

The difference in level between the predicted and the actual nitrogen content or degree of cyanoethylation is attributed to differences in the cyanoethylation processes as conducted at different times. Thus Figure 1 is not presented as a prediction nomograph, but rather as an indication of the correlation that may be established for each set of reaction conditions.

*Cyanoethylation of Pressure-Boiled Cotton Fibers*

Samples of the six cottons listed in Table I were pressure boiled and subsequently cyanoethylated under the same conditions as had been used for the raw fibers. The nitrogen analyses for cyanoethylated fibers are given in Table III. Correlation of the Micronaire fineness versus the nitrogen content again showed a negative and highly significant correlation coefficient at all times of reaction. The pressure-boiled samples exhibited somewhat higher correlations than the raw samples. It will also be noted from comparison with Table I that, in general, the extent of cyanoethylation is lessened by the boil for a given cotton and time of treatment. An exception is the highly immature (38%) Memphis cotton at 60 and 120 min. reaction.

*Cyanoethylation of Grey and Prior-Treated Thread*

In Table IV are shown the nitrogen contents obtained for various reaction times for samples of the grey and prior-treated 12/5 cotton thread. The degree of reaction for any given length of time is affected by the prior treatment. The comparison between the nitrogen content for the grey thread and the samples which had been pressure boiled or ethanolamine extracted show that below 6% the grey sample appears to react more rapidly. At the longer times of reaction, the rate for the pressure-boiled and ethanolamine-extracted samples accelerates, and higher nitrogen contents for the prior-treated samples are observed. Mercerization, which alters the accessibility, greatly increases both the rate and extent of cyanoethylation for all of the times observed. The ethanol extracted samples showed a small but persistently lower degree of reaction when compared with the grey yarn.

**TABLE IV. Cyanoethylation of 12/5 Cotton Thread Subjected to Various Prior Treatments**

| Time of treatment, min. | Grey, % N | Ethanol extracted, % N | Ethanolamine extracted, % N | Pressure boiled, % N | Mercerized slack, % N | Mercerized at constant length, % N | Spearman Rank Corr. Coefficient, $\rho_{t_{10}}$ |
|---|---|---|---|---|---|---|---|
| 10 | 3.1 | 2.9 | 2.6 | 2.5 | 5.2 | 3.9 | — |
| 20 | 3.7 | 3.6 | 3.8 | 3.3 | 7.0 | 6.7 | 0.83 |
| 30 | 4.0 | 3.9 | 3.9 | 3.8 | 7.7 | 7.5 | 0.99 |
| 60 | 6.1 | 5.9 | 6.1 | 6.4 | 9.6 | 10.2 | 0.50 |
| 120 | 7.3 | 6.8 | 8.3 | 7.9 | 11.2 | 11.1 | 0.54 |
| 180 | 8.8 | 8.1 | 9.5 | 10.7 | 12.2 | 12.2 | 0.47 |
| 240 | 10.2 | 9.8 | — | — | — | — | — |
| 360 | 11.2 | 10.3 | — | — | — | — | — |

Also in Table IV are listed the Spearman Rank Correlation Coefficients of the order of nitrogen content at various times compared with those of the order at 10 min. If 10 min. is used as the objective, it will be noted for times of treatment of 60 min. and longer that the correlation is reduced considerably. This is assumed to be further evidence that the rate of cyanoethylation not only differs because of prior treatment, but also changes in the course of cyanoethylation, resulting in such inversion, as may be noted in comparing the nitrogen contents of the raw and the ethanolamine-extracted samples at various times of treatment.

In other studies, purification has been noted to affect the reaction of cotton and beta-propiolactone [3]. It was shown that the presence of noncellulosic alkaline salts, naturally present in cotton, catalyzed the reaction, producing greater reaction in the grey than in the purified cotton. Cyanoethylation is also an alkali-catalyzed reaction and similar considerations might apply. In corroboration, the extent of reaction of pressure-boiled fibers (Table III) in virtually every case was less than that of the raw samples. However, no explanation is offered at this time for the apparent change in reaction rate of the pressure-boiled and ethanolamine-extracted yarn samples (Table IV), which resulted in these samples having a higher nitrogen content at the longer times of reaction than the grey.

Breaking strengths of the 12/5 thread plotted against nitrogen content are shown in Figure 2. While the controls have somewhat different breaking strengths, cyanoethylation to moderate nitrogen contents (4–8%) appears to reduce this variation. However, at the higher contents certain of the samples again showed divergence: the pressure-boiled and ethanolamine-extracted samples show a complete loss of breaking strength at approximately 10.5 and 9.5% nitrogen contents, respectively, whereas the other samples still retained a moderate amount of strength.

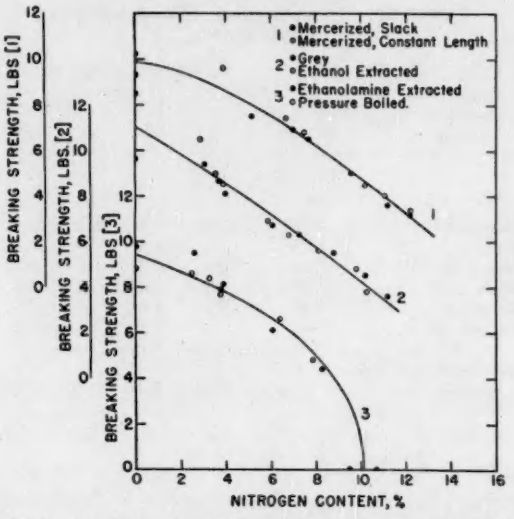


**Fig. 2.** Breaking strength versus nitrogen content for 12/5 sewing thread: grey and with various prior treatments.

### *Effect of Prior Treatment on the Rot Resistance of Cyanoethylated Cotton*

Samples of cyanoethylated cotton thread which had been subjected to different prior treatments were selected in the range of 3.8 to 4.0% nitrogen content and tested for rot resistance. This level of cyanoethylation has been found to provide adequate rot resistance for cyanoethylated grey cotton [6]. With the exception of the ethanol-extracted sample, none of the prior-treated samples were as rot resistant as the cyanoethylated grey thread (Table V). Prior treatments, other than ethanol extraction, tend to increase the accessible regions or change the caustic:

**TABLE V. Soil Burial of Selected Samples of Cyanoethylated Cotton Thread**

| Cyanoethylated cotton prior treatment | Nitrogen content, % | Original breaking strength, lb. | % Strength retained on soil burial | | |
|---|---|---|---|---|---|
| | | | 2 Weeks | 6 Weeks | 12 Weeks |
| Grey | 4.0 | 8.1 | 100 | 101 | 103 |
| Ethanol extracted | 3.9 | 8.5 | 95 | 98 | 97 |
| Ethanolamine extracted | 3.9 | 8.1 | 98 | 62 | 62 |
| Pressure boiled | 3.8 | 7.7 | 94 | 60 | 43 |
| Mercerized (const. length) | 3.9 | 9.6 | 80 | 23 | 0 |

water ratio in the fiber resulting in carboxyl formation [15].

While mercerization greatly accelerates the rate of cyanoethylation, the detrimental effect of this prior treatment is strikingly evident by the complete loss of rot resistance of the prior-mercerized cyanoethylated sample of 3.9% nitrogen content. In contrast, a prior-mercerized sample of 5.2% nitrogen content buried for 12 weeks retained 83% of its original strength. If mercerization is used as a prior treatment, higher degrees of cyanoethylation are needed to impart rot resistance.

## Summary and Conclusions

The rate and extent of cyanoethylation of cotton are affected by fineness as measured by the Micronaire. Highly significant rank correlations are observed between Micronaire fineness and nitrogen content for various times of treatment. It appears that the Micronaire fineness might serve as an index of the time necessary to attain a given nitrogen content, provided the process has been well standardized. Pressure boiling with 2% caustic as a prior treatment lowered the rate and extent of cyanoethylation.

Prior treatment of yarns also has a pronounced effect on the rate of the cyanoethylation reaction. Further, there is evidence that the rate for any given prior treatment does not remain uniform with reaction time or increasing nitrogen content.

At a fixed nitrogen content of approximately 4%, prior treatments were shown to influence the efficacy of cyanoethylation in promoting rot resistance. At this level of nitrogen, the cyanoethylated gray yarn withstood 12 weeks soil burial. Similarly the ethanol-extracted cyanoethylated cotton also withstood 12 weeks burial. Pressure boiling with 2% caustic or ethanolamine extraction apparently allowed some microbiological action to take place, because strength losses of approximately 50% were noted for this pair after 12 weeks. The mercerized sample completely disintegrated in this period. There was evidence that if mercerization is used as a prior treatment, higher degrees of substitution are needed to impart rot resistance by cyanoethylation.

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# Experimental Evaluation of the Lateral-Order Distribution in Cellulose[1]

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**Abstract**

The lack of agreement among various crystallinity and accessibility methods for cellulosic materials is explained in terms of the lateral-order distribution concept. A new definition of the order function is proposed which is more in keeping with recent infrared evidence showing that celluloses differ in distribution of hydrogen bond strengths rather than in actual number of hydrogen bonds.

Some of the physical and chemical methods which can give empirical-order distribution information for native and regenerated samples are reviewed critically and some data are compared with results based on conventional crystalline-amorphous delineation.

## Introduction

Conventional methods for evaluating the fine structure arrangement of cellulose fibers divide the material into two fractions: amorphous and crystalline [14]. This division, admittedly a first approximation which is convenient from an experimental viewpoint, fails to take into account important fine structure characteristics, such as the size of the crystalline regions and the contributions of regions of intermediate order to the supermolecular arrangement. Whether or not such omissions are justified must be judged in terms of the consistency of the data based thereon.

In Table I are assembled some representative crystallinity and accessibility values from the literature which show a decided lack of consistency. A more thorough compilation of the available data [24] serves only to emphasize that various methods for measuring the crystalline or accessible fraction of cellulose materials differ widely. To explain the discrepancy, several workers [23, 30] have suggested that material of intermediate order can behave either as crystalline or amorphous, depending on the method used. It is the purpose of the present paper to proceed still further in this direction with the hypothesis that the cellulose fine structure is made up of regions which show a statistical distribution of packing types.

Recently [15] this hypothesis has been given a qualitative statistical definition which appears to be more in keeping with experimental evidence. According to this definition, the crystalline regions are not necessarily alike in different cellulose fibers or even in separate regions of the same fibers, but the

[1] Paper presented at the Sixth Canadian High Polymer Forum, St. Catherines, Ontario, April 14–15, 1955.

**TABLE I. Noncrystalline and Accessible Cellulose Content, %**

| | Noncrystalline | | | Accessible | | |
|---|---|---|---|---|---|---|
| | Hydrolysis [7] | X Ray [12] | Density [13] | $D_2O$ [8] | Formylation [23] | Thallous ethylate [1] |
| Cotton | 6–8 | 30–31 | 40 | 44 | 12.5 | 0.4 |
| Wood pulp | 9–11 | 30 | 47 | 55 | — | — |
| Mercerized cotton | 11–14 | — | 60 | — | 20 | 3.3–27 |
| Fortisan | — | 51 | — | — | — | — |
| Fiber G | — | 47 | 54 | 67 | — | — |
| Textile rayon | — | 60–63 | 75 | 68 | 39 | — |
| High tenacity rayon | 27–31 | 60–61 | — | 86 | — | — |

molecular packing approaches to a greater or lesser degree the lattice arrangement of cellulose as determined by X-ray diffraction. "Crystallites" may differ in size, shape, or in degree of packing perfection, but in general for a given fiber sample there will be a most probable size and order which will depend on conditions under which the crystallization originally occurred. A complete definition of cellulose fine structure will require, therefore, a knowledge of the distribution of size, shape, and degree of perfection of the crystalline regions.

Similar reasoning must be applied to the "amorphous" and "mesomorphous" regions so that a definition of the entire supermolecular structure in terms of mass-order distribution results. At present this is beyond the scope of our experimental methods. However, there are a number of well-known physical and chemical properties of cellulose which can be adapted to give rough measures of order distribution in cellulose fibers. These methods will now be reviewed, and some data which have been obtained by the authors will be presented and compared with the results which are based on conventional crystalline-amorphous characterization.

**Fig. 1.** Schematic mass-order distribution in cellulose. $\bar{O}$ represents order, $q$ represents the quantity of cellulose existing at each order value.

### Characterization of Fringe Micellar Networks

To allow easier comparison between order measurements which are based on different techniques, the following statistical outline[2] is presented. Let us consider a structure as shown in Figure 1 and choose some volume $V$, the only restriction being that it is greater than the cellulose unit cell yet smaller than any volume of crystallized material which would behave as an infinite crystal. If $V$ is placed at some point in the structure as origin, it will encompass a certain number of glucose residues for which a degree of order $\bar{O}$ can be defined by the equation

$$\bar{O} = \frac{[OH_e]}{[OH_t]}$$

where $OH_e$ is the total number of hydrogen bonds in the region and $OH_t$ is the total possible number of hydrogen bonds if all the molecules were perfectly crystallized. Thus $\bar{O}$ is a measure of packing perfection in the volume $V$ with limits $0 \leq \bar{O} \leq 1$. If $V$ is translated unitwise in all directions through the fiber, it will encompass other degrees of order $\bar{O}_1, \bar{O}_2, \bar{O}_3$, in the direction of increasing order, with statistical repetition of identical orders and the whole structure can be represented as a spectrum of order as shown in Figure 1. The fraction of cellulose with order corresponding to $\bar{O}_i$ is $q_i$ and similarly quantities $q_1, q_2 \cdots q_n$ can be associated with $\bar{O}_1, \bar{O}_2, \bar{O}_3 \cdots \bar{O}_n$. Expressingt hese quantities summatively, one obtains the expression

$$Q_n = \sum_{i=0}^{i=n} q_i$$

where $Q_n$ is the amount of cellulose with order up to and including $\bar{O}_n$. A summative curve, as depicted in Figure 2A, is obtained when values of $Q$ are plotted against the equivalent $\bar{O}$ values. Differentiation of the summative curve yields the distribution curve of Figure 2B which gives the fraction of material with order $\bar{O}_n$. Thus, a highly crystalline fiber with relatively limited amorphous regions would be consistent with curve 2, while a fiber rich in disordered material with curve 1.

It is interesting to note how critical, even in theory, is the size of the volume element. If this volume is too small, then the depicted curves split

[2] The statistical outline immediately following is based on a similar presentation in Chapter IV B of "Cellulose and Cellulose Derivatives," edited by E. Ott and Harold M. Spurlin, written by John A. Howsmon and Wayne A. Sisson; Interscience Publishers, 1954.

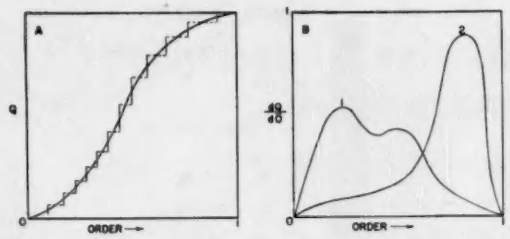


**Fig. 2.** (A) Summative mass-order curve for lateral order in cellulose; (B) schematic lateral-order distribution curves for cellulose: (1) low lateral order; (2) high lateral order.

into two sharp peaks at zero order and perfect order; if too large, then a single sharp peak appears at a value of $\bar{O}$ corresponding to an over-all average. In practice, the small volume is analogous to an arbitrary definition of crystallinity which places all material in one class or another; the summative quantities so defined are

$$Q_a = \sum_{i=0}^{i=k} q_i \quad \text{and} \quad Q_c = \sum_{i=k+1}^{i=n} q_i$$

where $Q_c$ is the percentage of crystalline cellulose and $Q_a$ the percentage of amorphous cellulose present. In the same terms, various methods for measuring crystallinity will agree only if the quantity summation limits are the same. The choice of too large a volume to define lateral order is analogous to the choice of a single fiber parameter, e.g., density to define the order level.

The above definition of the order function has been criticized [20] on the basis that not all hydrogen bonds contribute equally to the cohesive energy of the unit volume. Recent studies of the infrared spectra of cellulosic materials show that few if any of the hydroxyls groups are not involved in some sort of H bond [20]. The predominant fine structure characteristic of these materials is apparently not the number distribution of hydrogen bonds but their intensity distribution. The infrared data also suggest that a not inconsiderable number of the hydrogen bonds may be intramolecular so that they do not contribute to the bonding energy of the crystal. In view of these criticisms, a more exact definition of the order function seems desirable, but until our knowledge of the forces which are responsible for the cohesion of the cellulose structure is more developed the only exact definition of $\bar{O}$ can be thermodynamic. Thus following Chedin [6], we may characterize each of the unit volumes by a certain heat of fusion $E_r$, the energy which must be supplied to the unit volume to bring it from its native state to the completely amorphous state. For each unit volume, $E_r$ will be a function of the type, strength, and number of H bonds and other intermolecular forces.

Although conceptually the thermodynamic definition is not so clear-cut as the original, it does have the merit of not contradicting known facts and of being amenable to direct experimental evaluation.

### Physical Methods

The ideal method for characterizing the fiber according to mass-order would be one which does not modify the fiber in any way and which from a single measurement gives the complete order distribution. This definition immediately suggests the use of a physical method such as X-ray diffraction. However, at present only very qualitative information regarding order distribution can be obtained from X-ray measurements without modifying the sample. The physical methods which are most adaptable to evaluation of lateral-order distribution are those which allow stepwise modification of the fine structure. At each step the increment in some fiber property, which is a function of order, is determined and is plotted against the intensive factor which brought about the variation. Thereby a curve is obtained which corresponds to the summative curve described above. If the intensive variable is assumed to be a linear function of order, then the rate of change of the fiber property at any order level is a measure of the amount of material with corresponding order. Thus, the distribution curve is obtained by plotting the slope of the summative curve against the order function.

All systems whose swelling power for cellulose increases regularly with concentration can probably be adapted for definition of mass-order distribution in this manner. The best known example is, of course, the sodium hydroxide–water system. That aqueous sodium hydroxide solutions of increasing strength can penetrate regions of increasing order may be deduced from consideration of the heat of mercerization [22], the X-ray diagram and moisture regain [25], and the hydrolysis behavior [17] of the sample after treatment with caustic solutions of varying strength. Over a particular concentration range all of these properties show gradual transitions to the values characteristic of the mercerized state.

In the present study, a 2-g. sample of "fluffed" cellulose was steeped for 1 hr. in 60 ml. of carbonate-free sodium hydroxide solution at 27.0 ± 0.1°C. in a stoppered flask. Afterward the mixture was flooded with distilled water at room temperature, and a filter stick was used to remove the water rapidly. After three such washings, the sample was allowed to stand for 15 to 25 min in 2% acetic acid; it was then filtered on a tared sintered glass filter and washed until neutral. From the oven-dry weight of the residue, the amount of dissolved cellulose was calculated. Sodium hydroxide solutions ranging from 0 to 16% by weight were used in the steeping process. The corresponding change in lateral order was determined by measuring the change in moisture regain at 58 or 64% R.H. according to a procedure previously described [16].

An alternative method which was used for determining the changes in lateral order consisted in measuring the heat evolved by the reaction between cellulose and the aqueous caustic solutions. An isothermal "Bunsen type" calorimeter, with diphenyl ether as working fluid, was used for this purpose [2]. All cellulose samples used were dried under vacuum over $P_2O_5$ at 100° C. and were stored in vacuum-sealed glass capsules which were broken open inside the calorimeter.

*Order Distribution from Regain*

In Figures 3 and 4A the loss in weight and regain values are plotted, respectively, against sodium hydroxide concentration for three native cellulose samples: acetate-grade cotton linters, a prehydrolyzed sulfate pulp, and a sulfite pulp.

The regain curve which is characteristic for this kind of treatment has been reported by a number of investigators [17, 21, 25, 27], and as they have emphasized, the position of the inflection point is an important index of fine structure which depends on the source of the cellulose and the method of isolation and purification. Thus the concentration of sodium hydroxide at which a relatively large increase in regain begins is least for the sulfite pulp, increases for the sulfate pulp, and is greatest for the linters sample. The rate of change of regain and the degree of change are reflected in the height and width of the derived distribution curves in Figure 4B.

In terms of the lateral-order concept, the distribution curves show that cotton ranks first in degree of order, the sulfate pulp second, and the sulfite pulp third. This follows from the position of the maximum relative to the abscissa, sodium hydroxide concentration, which is considered as a measure of order. Another important characteristic is the breadth of the peaks or the root mean square deviation, which

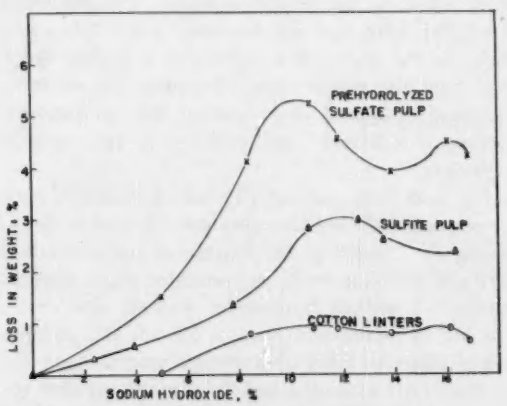


**Fig. 3.** Per cent loss in weight for various cellulose samples after steeping in sodium hydroxide solution.

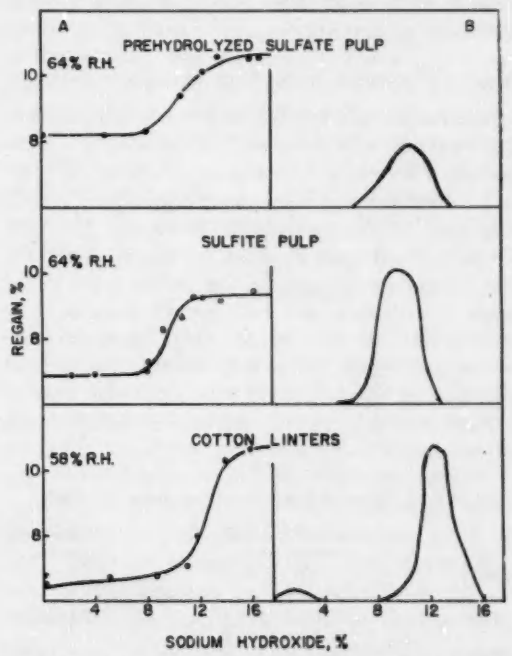


**Fig. 4.** (A) Per cent regain at a fixed relative humidity for celluloses after steeping in sodium hydroxide solution. (B) Mass-order distribution curves derived from the slope of the corresponding regain curve.

is a measure of heterogeneity of the polymorphic structure. That is, within an arbitrary unit volume translated unitwise throughout the entire fiber, the probability of variation in the defined order function $\bar{O}$ from the average value is least for cotton, and so forth. . . . This is in keeping with the well-known observation that the sulfate pulps generally show greater resistance to swelling and lower reactivity than sulfite pulps, while cottons rank ahead of all wood cellulose in this respect [9]. However, there are special sulfite pulps whose order-distribution curve is nearly indistinguishable from that of a prehydrolyzed sulfate pulp.

The sodium hydroxide swelling-regain method is generally applicable to natural cellulose fibers, but is not particularly useful for regenerated fibers because of crystallization and solubility effects. Even with natural fibers the differentiation is sharp only in the regions which possess a high level of order. This is not unexpected since the regain of a low order region should not change significantly upon swelling and drying. For this reason, despite the simplicity of the regain method, a more direct measurement such as the heat of mercerization is to be preferred.

*Order Distribution from Heat of Mercerization*

In Table II are recorded some heats of mercerization (the heat evolved when 1 g. of bone-dry cellulose reacts with an excess of aqueous sodium hydroxide) for the cotton linters and prehydrolyzed sulfate pulp used in the previous experiments. The data are plotted in Figure 5. Like the regain values, the heat effects are greater for the sulfate pulp in the range investigated, and both curves increase with concentration in this region. The larger increase for the sulfate pulp can be only tentatively associated with greater disorder since the measured heat of mercerization involves (i) the heat of reaction with sodium hydroxide and (ii) the heat of phase change from order to disorder. Further work is required to separate these various components since our interest lies mainly in the latter heat effect.

**TABLE II. Heat of Reaction of Cellulose with NaOH**

| % NaOH | Prehydrolysed sulfate pulp $-\Delta H$ cal./g. | Acetate-grade linters $-\Delta H$ cal./g. |
|---|---|---|
| 0.00 | 13.7, 13.6, 13.3 13.4, 13.4, 13.6 | 11.1, 11.2 |
| 2.06 | 15.0, 15.6 | 12.2, 12.1 |
| 3.51 | 16.4, 16.2 | 12.8 |
| 5.01 | 17.3, 16.9 | 13.8, 13.6 |
| 6.63 | 19.1, 18.9 | 15.0, 14.8 |
| 8.43 | 19.5, 19.9 | 15.0 |

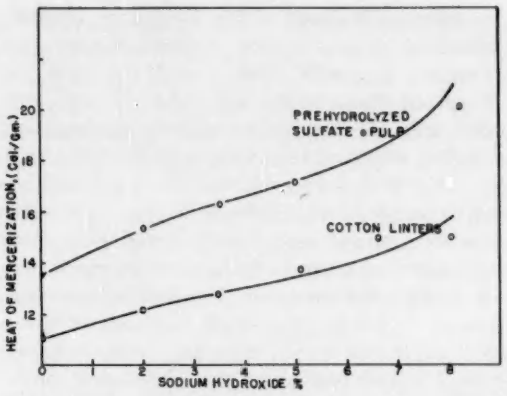


**Fig. 5.** Heat of mercerization (cf. text) for prehydrolysed sulfate and cotton linters cellulose in sodium hydroxide solution.

*Order Distribution by Other Methods*

The effect of sodium hydroxide on the mercerized fiber can be followed by X rays [25] and by viscosity determinations after hydrolysis (levelling off degree of polymerization) [3, 17]. While it is difficult at this stage to classify methods according to merit, a number of factors suggest that neither of these is as satisfactory as the regain or heat of mercerization procedures for evaluation of mass-order. The former is open to the usual criticism of X-ray methods that there is a lower limit to the crystal size or degree of order which is discernible as such. The published data [25] bear this out for they would place the peaks in the distribution curves at a higher order level than the regain data. Furthermore no truly quantitative method of evaluating the relative proportions of cellulose I and cellulose II are available at present.

The hydrolysis method [3], which combines both the physical and chemical approach, consists in determining the "levelling off" degree of polymerization ($\overline{DP}$) of a sample which is pretreated in an aqueous solution of sodium hydroxide, washed, and dried. The $\overline{DP}$ is determined after 4, 10, 15, and 20 min. of hydrolysis in 2.5*N* hydrochloric acid at 105° C.; the values are averaged and the average negative increment in $\overline{DP}$ at each concentration of sodium hydroxide is used to obtain the summative curve. On

a relative basis hydrolysis gives mass-order results which are similar to the regain method, but it is unnecessarily indirect and introduces the additional variable of hydrolysis.

Still another method which depends on the swelling properties of sodium hydroxide solutions is the hydrocellulose solubility method reported recently by H. Maeda [19] and T. Yurugi [31] and applied extensively to native and regenerated fibers. After hydrolysis under mild conditions but for a relatively long period the hydrocellulose is washed and dried and the graded solubility of the dry material in sodium hydroxide solution is measured. The amount of material which is soluble at each NaOH concentration corresponds to the summative quantity $Q$, and the summative curve is obtained by plotting $Q$ versus concentration (usually up to 8%). The method appears to be one of fractional solution of the crystallites according to crystal size or crystal perfection. For regenerated fibers whose hydrocellulose residue is almost completely soluble in 8% NaOH, the method appears useful but again rather indirect. A sample of some of the distribution curves derived therefrom is in Figure 6.

In all the foregoing methods employing aqueous NaOH as swelling agent, the results have been evaluated on the assumption that the swelling power or mercerizing ability of sodium hydroxide is a linear function of the weight per cent concentration. If we consider the process as equivalent to the dissolution of a solid in a liquid, then the free energy condition which must be satisfied in order for a given unit volume of cellulose to be completely penetrated (mercerized) by the alkaline solvent is

$$\Delta G = E_r + \Delta H - T\Delta S < 0$$

$\Delta G$ is the sum of the free energies of the hypothetically separate processes of melting the solid to the supercooled liquid and mixing the liquid with the solvent.

$E_r$ is the heat of fusion per unit volume; it is positive and greater the closer the unit volume is to perfect order.

$\Delta H$ is the enthalpy of mixing of the hypothetical liquid with the NaOH solution. It is negative.

$\Delta S$ is the entropy of the process including fusion and mixing and is almost certainly positive.

Clearly penetration or mercerization for any region of the fiber can occur only if $\Delta H - T\Delta S$ is negative and of sufficient magnitude to make $\Delta G < 0$. Recent consideration of the sodium hydroxide–cellulose interaction [6] suggests that $\Delta H$ is the predominant factor in the process and that it increases faster than in direct proportion to the weight per cent concentration of sodium hydroxide. Accordingly, the above assumption is not strictly valid, but it hardly changes the relative character of the results. For regions of low order, $E_r$ is only slightly greater than zero and the sodium hydroxide concentrations at which $\Delta H$ is sufficiently large are relatively small, but when $E_r \gg 0$ greater concentrations of alkali are required to achieve penetration. Therefore, the statistical distribution of $E_r$ values is the true measure of the lateral-order distribution.

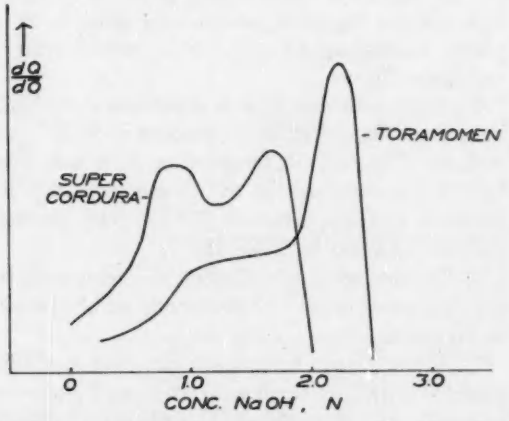


**Fig. 6.** Lateral-order distribution curves for Toramomen and super cordura rayon according to H. Maeda [19].

## Chemical Methods

Chemical methods for defining the lateral-order distribution of cellulose are based upon the measurement of a chemical property of the fiber as a function of some reaction variable, such as temperature or concentration of reactant, with the idea that increasing the severity of the conditions causes a shift in the equilibrium to include material of increasing order. The formic acid esterification of cellulose which has been used by Nickerson [23] and Tarkow and Stamm [28] and later by Troitzsch [30] to measure chemical accessibility is the kind of reaction which can readily be adapted to give mass-order information since the degree of formylation is a function of temperature and concentration. Although there is evidence that some degradation does occur due to

this reaction, there should be virtually no recrystallization and therein lies its chief virtue.

Another example of the same reaction type is the nitric oxide oxidation of cellulose [26], where it has been shown that the degree of oxidation is extremely concentration-dependent.

In the present investigation the formylation method was used exclusively. Since the literature [23, 28] shows disagreement both in regard to experimental results and reaction mechanism, an independent investigation was undertaken in this laboratory, and the following conclusions were reached:

1. Formylated celluloses are sufficiently stable to heat and moisture to allow normal handling procedures without excessive formyl losses. However, saponification does occur on standing a number of days at room temperature.

2. Slightly beyond a formic acid to cellulose ratio of four, the rate of formylation becomes constant. The observation that the extent of substitution becomes constant when the swelling in formic acid is equivalent to the swelling in water at the fiber saturation point [28] was not confirmed in this investigation.

3. The experimental curves in Figure 7 show clearly that rayons esterify more rapidly than native celluloses such as wood pulp, and in all cases the rate of esterification is initially very rapid, but proceeds at a decreasing rate. Therefore comparison of the extent of reaction for two celluloses under identical experimental conditions provides a relative measure of the degree of accessibility. By assuming that a material such as white dextrin or starch is 100% accessible, the accessibility scale is conveniently calibrated for any time of reaction. This is the technique employed by Nickerson [23] which was also used in this investigation.

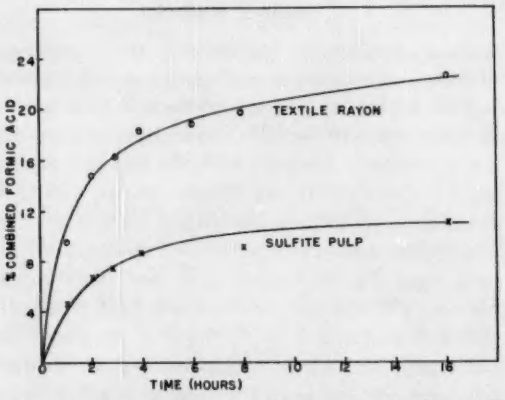


**Fig. 7.** Combined formic acid, in per cent, for textile rayon and sulfite pulp at various times; weight ratio formic acid to cellulose of 1, temperature 55° C.

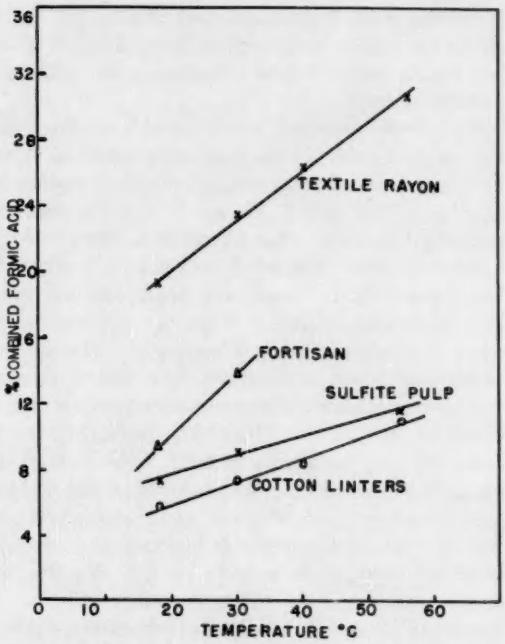


**Fig. 8.** Combined formic acid, in per cent, after 16-hr. reaction at various temperatures; weight ratio formic acid to cellulose of 1.

4. The rate of esterification of cellulose in formic acid increases with temperature, as shown in Figure 8, where the degree of esterification after 16 hr. is plotted against temperature; otherwise the reaction appears unchanged.

5. Appreciable degradation of cellulose occurs during formylation. For 16-hr. reaction in 98% formic acid the drop in D.P. ranges from 12% for rayon to 28% for wood pulp at 18° C. and from 21% for rayon to 41% for cotton at 55° C. The pertinent data are collected in Table III.

6. The degree of esterification decreases with increasing water content of the formic acid, as shown in Figure 9.

7. Although most formylation experiments yielded products with less combined formic acid than that required for a cellulose monoformate (24.2% HCOOH), it was found possible to prepare cellulose

formates with a degree of substitution of 1.3 (30.0% HCOOH) without the use of a catalyst. This is contrary to some statements in the literature [10, 28] which assert that cellulose will form only a monoformate by esterification of the primary hydroxyl at position 6. More recently Browning and Sell [5] found that the esterification of starch and cotton linters proceeds well beyond the monoformate stage when the ratio of formic acid to carbohydrate is sufficiently large.

**TABLE III. Degradation of Cellulose by Formic Acid**

| Sample | Original D.P. | D.P. 16-hr. reaction |
|---|---|---|
| A. 55° C. HCOOH/Cellulose Ratio = 1 | | |
| Cotton (acetate grade) | 1153 | 702 |
| | | $677\left(\frac{\text{HCOOH}}{\text{Cell.}} = 2\right)$ |
| Sulfite pulp | 1377 | 826 |
| Textile rayon | 441 | 347 |
| B. 18° C. HCOOH/Cellulose = 10 | | |
| Cotton linters (acetate grade) | 1153 | 973 |
| Sulfite pulp | 1377 | 1057 |
| Textile rayon | 430 | 380 |

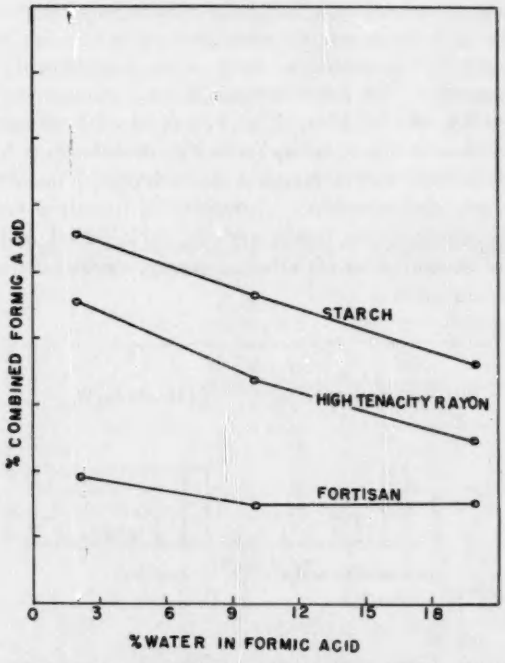


**Fig. 9.** Combined formic acid, in per cent, after 16 hr. at 18° C. with varying amounts of water in formic acid; weight ratio of formic acid to cellulose of 10.

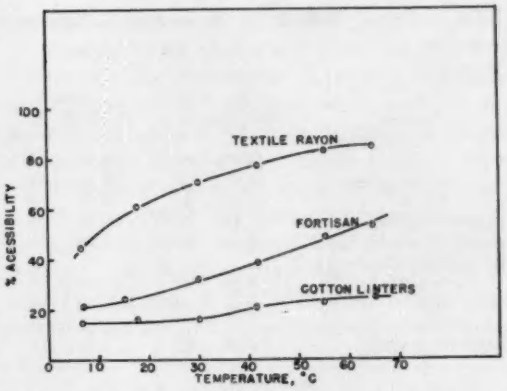


**Fig. 10.** Per cent accessibility based on starch, versus temperature for different cellulose samples.

On the basis of the preceding data, the following procedure was adopted to evaluate the relative accessibility of various celluloses to formic acid:

1. Approximately 5 g. of cellulose was dried in vacuo at 65° C. and weighed.

2. Sufficient 90% HCOOH was added so that the ratio of formic acid (dry basis) to cellulose was 10:1.

3. The reaction was quenched after 16 hr. by addition of a large amount of distilled water at room temperature. The samples were then washed free of excess formic acid with water and air-dried.

4. A modified Eberstadt method was used to analyze for combined formic acid, and results were expressed as the per cent accessibility based on the degree of substitution of the sample compared with that of the soluble starch calibration sample.

Starch samples which were soluble in the formic acid required special treatment in step 3 above. The reaction was quenched by the addition of absolute ethanol and the product washed free of excess formic acid by an 80–20 ethanol-water mixture.

Temperature was chosen as the reaction parameter to obtain mass-order information from the formylation data. Accordingly, the reaction was carried out at 7, 18, 30, 42, 55, and 65° C. The results are recorded in Table IV. Figure 10 shows the effect of temperature on the accessibility of various celluloses relative to starch. The accessibility is largest for the regenerated celluloses which, of course, possess the greatest amount of disorder.

**TABLE IV. Accessibility of Cellulose in 90% Formic Acid at Various Temperatures**

| Sample | 7° C. | | 18° C. | | 30° C. | | 42° C. | | 55° C. | | 65° C. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % HCOOH | % A | % HCOOH | % A | % HCOOH | % A | % HCOOH | % A | % HCOOH | % A | % HCOOH | % A |
| Starch | 24.35 | 100 | 27.32 | 100 | 29.65 | 100 | 29.79 | 100 | 30.40 | 100 | 31.07 | 100 |
| High tenacity rayon | 13.23 | 51 | 21.00 | 73 | 24.02 | 77 | 27.86 | 94 | 29.08 | 94 | 29.52 | 94 |
| Textile rayon | 11.54 | 44 | 17.29 | 60 | 21.99 | 70 | 24.07 | 77 | 25.86 | 82 | 26.78 | 84 |
| Experimental rayon | 9.12 | 34 | 14.45 | 49 | 17.78 | 56 | 22.53 | 72 | 24.88 | 78 | 25.96 | 81 |
| Fortisan | 5.89 | 21 | 7.59 | 24 | 10.66 | 32 | 12.71 | 38 | 15.98 | 48 | 18.11 | 53 |
| Mercerized cotton linters (acetate grade) | 8.54 | 32 | 11.55 | 38 | 13.96 | 43 | 15.78 | 48 | 17.79 | 54 | 17.23 | 50 |
| Sulfite pulp | 5.23 | 19 | 6.19 | 19 | 7.58 | 22 | 9.13 | 27 | 9.49 | 27 | 10.60 | 30 |
| Cotton linters (acetate grade) | 4.17 | 15 | 5.49 | 16 | 6.03 | 16 | 7.38 | 21 | 7.83 | 22 | 8.67 | 24 |

Conversion of these data into a lateral-order distribution cannot be carried out as for the regain method; first because there is no conveniently defined "zero order" level corresponding to 0% NaOH, and second because the summative curve which would be defined by a plot of per cent accessibility to formic acid against temperature would not include all of the material at the highest temperature used in these measurements. Accordingly, the results are broken into seven fractions, each one defined to include material of increasing order. Thus fraction 1 is defined as the per cent cellulose accessible to 90% formic acid at 7° C., fraction 2, as the per cent cellulose accessible at 18° C. which was not accessible at 7° C., etc. Proceeding in this fashion, the data of Table IV were assembled and plotted in histogram form in Figures 11 and 12. Qualitatively, for the native samples these results agree with those obtained from the study using aqueous alkali for cotton and wood pulp. It is immediately apparent, however, that these two methods are complementary rather than correlative. While formylation shows up structural variations in the low order regions, which were hitherto not observable, and which are of special interest in the case of regenerated celluloses, it is quite uninformative concerning the relative order in the "nonreactive" portion of the fiber. At this point, the sodium hydroxide–regain method provides an answer as to breadth of distribution and order level. Thus the nearly similar amounts of material in fraction 7 for the acetate-grade linters and the sulfite wood pulp are shown to be of different average order by the regain method.

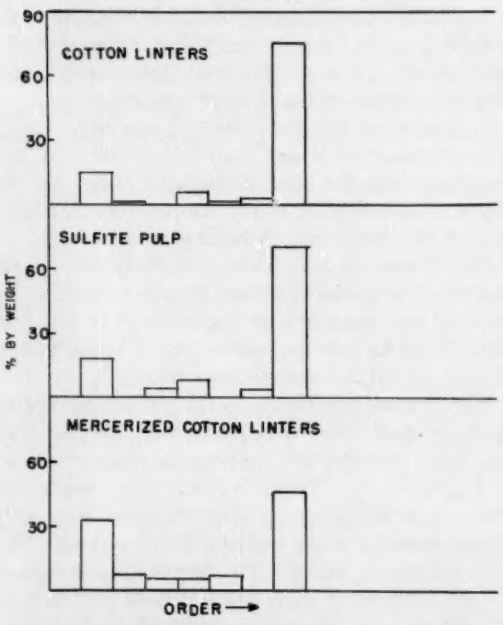


**Fig. 11.** Histogram plot of mass-order distribution from formylation data. Per cent by weight versus order.

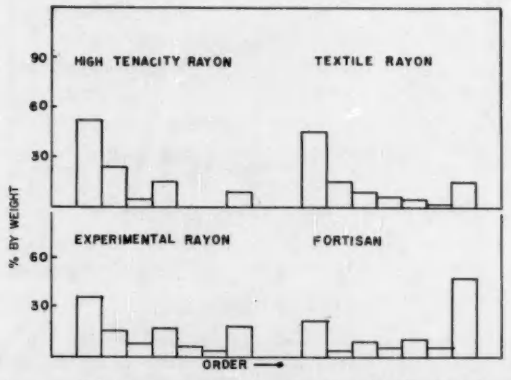


**Fig. 12.** Histogram plot of mass-order distribution from formylation data. Per cent by weight versus order.

In terms of our statistical model above, it must be concluded that the formylation method applied to native celluloses is not definitive enough (the volume element is too small); hence the distribution falls mainly into the two end fractions. It is interesting, however, to note the shift in the distribution that occurs when cotton is mercerized, which shows clearly that mercerization is mainly a transition from order to disorder.

The experimental results for the rayon samples are most easily interpreted by means of comparison with conventional per cent accessibility and per cent crystallinity values. The pertinent data are arranged in Table V, where the formylation values are expressed as the material in fractions 1 to 6 and the material in fraction 7. The similarity of the per cent accessibility and the amount of material falling in fractions 1 to 6 suggests that the chief virtue of the formylation method is that it allows detailed classification of the low order regions which constitute 60 to 85% of most regenerated fibers. In view of the large differences in properties of these fibers, this information should prove valuable in relating end use to fine structure.

To illustrate the chemical method still further, some data of Roseveare and Spaulding [26] for the oxidation of cellulose with $NO_2$ dissolved in carbon tetrachloride are tabulated in Table VI. All values are for a fixed time of reaction, 33.1 hr. at 25° C., and were obtained by interpolation. It is assumed that the only reaction involved is oxidation at the number six carbon atom of the glucose molecule. The corresponding histogram plots are shown in Figure 13. The distribution of material among the several blocks is in good agreement with the formylation histograms for high tenacity rayon and cotton linters showing that either temperature or reagent concentration can serve the same purpose, namely overcoming the energy barrier which the crystalline cohesion of the cellulose presents to any reactant. The thermodynamic reasoning which was applied to the case of the cellulose-alkali reaction is equally applicable in the present case.

**TABLE V. Comparison of Accessibility-Crystallinity Data with Order Distribution by the Formylation Method**

| Sample | Moisture regain [16] | | Formylation | |
|---|---|---|---|---|
| | % Accessibility | % Crystallinity | % in fractions 1–6 | % in fraction 7 |
| Fortisan | 63 | 51 | 53 | 47 |
| Experimental rayon | 75 | 35 | 81 | 19 |
| Textile rayon | 79 | 29 | 84 | 16 |
| High tenacity rayon | 87 | 18 | 91 | 9 |

**TABLE VI**

| Concentration $NO_2$, % | % Oxidized | |
|---|---|---|
| | Tire cord | Cotton |
| 4.0 | 46 | 24 |
| 8.0 | 70 | 30 |
| 12.0 | 85 | 35 |
| 16.0 | 98 | 40 |

## Discussion

The general concept of lateral-order distribution was proposed over a decade ago [11] and, significantly, was first championed by workers in the field of cellulose derivatives. In the interim there have been numerous indications that investigators were aware of the fallacies of oversimplifying the supermolecular architecture of the fiber [8, 16, 23, 30]. However, despite the large discrepancies in the estimates of crystallinity obtained by various procedures, which suggest that transition areas are important in

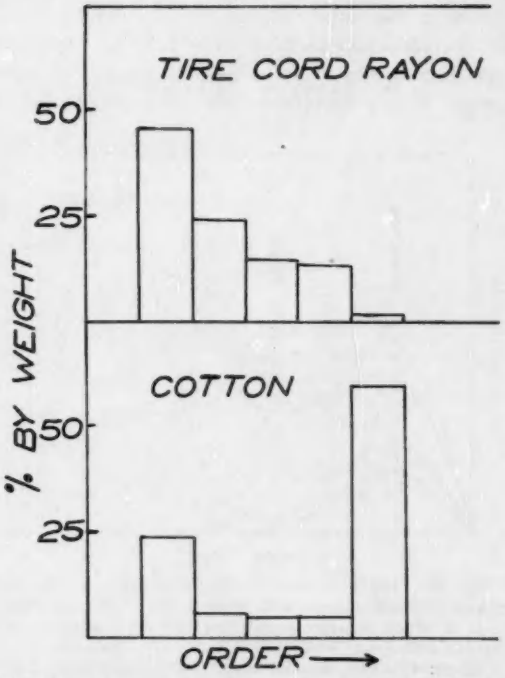


**Fig. 13.** Histogram plot of mass-order distribution from $NO_2$ oxidation data. Per cent by weight versus order.

the over-all picture, division of the fiber into two opposing fractions will undoubtedly continue. This is so not only because it is convenient from an experimental viewpoint, but also because experimental results especially from hydrolysis, X-ray, and density measurements can be interpreted in terms of a sharp transition from crystalline to noncrystalline [18]. From the preceding data it does appear that for native fibers this may be an acceptable approximation, but not for regenerated fibers. Accordingly the order-distribution concept is proposed as a more unified cellulose structure theory.

The lateral-order distribution hypothesis can be used to explain a great deal of the apparently anomalous crystallinity and accessibility data, some of which are collected in Table I. The observed differences in the crystallinity values are due to the fact that the various methods do not define crystallinity at the same order level. As stated above, this is equivalent to a difference in the quantity summation limits. Accordingly if the tentative lateral-order curves which have been proposed [15] are plotted on the same order scale, then it should be possible, as shown in Figure 14, to draw a line at some order level which will divide the areas under the various curves in the same ratio as the accessibility result for the particular method. The lines in Figure 14 have been drawn at approximately the correct positions. It is evident therefrom that comparison of accessibility data derived from various methods can provide a rough measure of order distribution.

From a practical viewpoint, the formylation and $NO_2$ methods applied to regenerated celluloses are perhaps the most interesting of the above data. Manufacturing variables allow the production of rayons of widely differing properties which can only be related to fine structure by careful "fingerprinting" as these methods allow.

In this paper an attempt has been made to adapt some known physical and chemical properties of cellulose to the measurement of order distribution. The methods described are not the only ones available nor necessarily the best ones, and because of the empirical methods of obtaining the order-distribution curve, the results obtained from various methods will not be directly comparable. However, the general character of the distributions should be comparable as appears to be the case for the formylation and nitrogen dioxide methods above. Under any circumstances characterization of a sample according to its order-distribution curve will be more useful than simple differentiation on the basis of crystallinity or accessibility alone. The ultimate objective should be a distribution curve based on a thermodynamic definition of order such as the cohesive energy density of the unit volume.

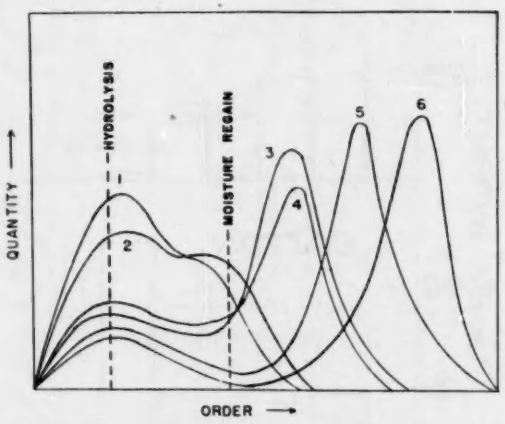


**Fig. 14.** Tentative lateral-order distribution curves for various cellulose fibers with broken lines showing order levels at which moisture regain and hydrolysis methods distinguish between crystalline and amorphous material.

Curves: (1) high tenacity rayon; (2) textile rayon; (3) high strength, low-elongation rayons; (4) mercerized native fibers; (5) wood pulps; (6) cotton.


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# The Treatment of Wool with Acid Bromate Solutions

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**Abstract**

A study has been made of the reaction of acid bromate solutions with wool. In hydrochloric acid solution, bromate and chloride ions react to give a mixture of bromine and chlorine, the halogens then reacting with the wool to produce unshrinkability. The reaction is activated by the addition of strong reducing agents, and in the majority of cases part of the bromate is reduced to bromide, the bromide then reacting with unchanged bromate to produce bromine. In the case of reactions involving aldehydes such as formaldehyde and glyoxal, a different mechanism is probably involved since addition of moderate amounts of silver salts does not affect the rate of reaction or the degree of unshrinkability produced.

## Introduction

The earliest methods for rendering wool nonfelting were all based on the use of chlorine, either as such or as hypochlorite. These methods suffer from many defects, one of the most important being the rapid rate of reaction of chlorine with wool. Attempts have therefore been made to find other reagents, and since chlorine is a powerful oxidizing agent, much

attention has been paid to the reaction of wool with other oxidizing agents. Among the more important oxidizing agents proposed for rendering wool unshrinkable are bromine [20], fluorine [23], permanganate [11], N-halogen compounds [19], permonosulphuric acid [18], chlorite [14], and bromate [15], and detailed studies have been made of the action of fluorine [10], permanganates [4], N-halogen compounds [1, 2], and chlorite [7].

A study of the reaction of chlorite solutions with wool showed that it was possible to activate the reaction in neutral solution by using aldehydes, particularly formaldehyde, and strong reducing agents [7]. In this paper a study has been made of the reaction of acid bromate solutions with wool. The reaction is activated by formaldehyde and glyoxal and by strong reducing agents.

## Experimental

### *Materials*

The wool used was a twofold 18s yarn of 56/58's quality knitted into fabric, using 12 needles and 18 courses per inch. Before use the wool was given a scour in soap and ammonia at 40° C. followed by a thorough rinse in water. Single squares of wool weighing approximately 5 g. were used for the majority of treatments.

Where possible, the chemicals used were of "Analar" or similar specification. Formaldehyde was used in the form of a 40% (wt./wt.) aqueous solution.

### *Wool Treatments*

The fabric was wetted-out in 1% aqueous Dispersol VL. (I.C.I.), washed, and squeezed. It was then sewn onto a glass stirrer, driven at 100 r.p.m. (unless otherwise stated), and entered into the reaction mixture. After the reaction was completed, the samples were treated for 1–2 min., with a very dilute sodium bisulphite solution to remove any residual oxidizing agent present in the wool. Unless stated otherwise, all concentrations are expressed as the percentage weight of the reagent on the weight of wool treated.

### *Shrinkage Testing* [6]

Shrinkage tests were carried out by hand milling in a 1% soap solution at 30° C., after allowing the samples to recover from mechanical stress by immersing in the soap solution for at least 1 hr. before milling.

### *Alkali Solubility* [9]

The sample, of known dry weight, was treated for 1 hr. at 65° C. with 0.1*N* sodium hydroxide at a liquor ratio of 100:1. The wool was recovered in a Buchner funnel, washed free from alkali, and dried to constant weight. The alkali solubility is expressed as the percentage loss in weight.

Before carrying out the alkali solubility test, the samples were just neutralized with dilute ammonia to remove any excess acid present, as the majority of the bromate treatments were carried out in 0.10*N* acid solution.

### *Analytical Procedure*

Bromate was determined by allowing the solution to react with excess of potassium iodide solution in 1–2*N* sulphuric acid. Under these conditions the reaction

$$HBrO_3 + 6HI \rightarrow HBr + 3H_2O + 3I_2$$

is quantitative within 15–20 sec.

The progress of the majority of the wool treatments carried out was followed by titrating aliquot portions of the bath with 0.05*N* or 0.02*N* sodium thiosulphate, after liberating the iodine by the above method. From the initial strength of the bath and the titration figures obtained during treatment, the half-life of the reaction was calculated. The half-life is a convenient measure of the rate of the reaction.

The titration figures, obtained as above, represent the total oxidizing power in the solution at any given time. From the appearance of the solutions, however, it was obvious that some free bromine was present. The amount of bromate present at any time was determined by adding 10 ml. of a 6% aqueous phenol solution to 25 ml. of the bath diluted with an equal volume of water. This removes any free bromine as 2:4:6 tribromophenol without reacting with the bromate. The bromate was then estimated by addition of acid and potassium iodide, as described above. Provided the liberated iodine was titrated with thiosulphate within 2 min., the phenol present did not interfere in the estimation of the bromate.

The difference between the total oxidizing power and that due to bromate was assumed to be due to free bromine. This was shown to be correct by estimating the free bromine colorimetrically using a Spekker photoelectric absorptiometer.

The amount of free halogen present in the solution at the half-life is expressed as a per cent of the

total oxidizing power present in the solution at the time. This figure probably gives an indication of the evenness of the treatment, since the greater the amount of free halogen present, the more the process approximates to an uncontrolled halogenation, which is known to give unlevel treatment.

The formaldehyde content of a completely exhausted bath was determined by adding an excess of neutral sodium sulphite solution to an aliquot portion of the bath neutralized to thymolphthalein and titrating the liberated alkali with standard acid solution [12]. Attempts were made to use this method to estimate the formaldehyde content of the bath during the reaction with wool, but great difficulty was experienced in detecting the end point, a gradual transition from dark blue through light blue to colorless being obtained over a titration range of 3–4 ml. 0.1*N* acid, instead of the usual one spot color change. This was found to be due to reaction between the free bromine in solution and the indicator. The difficulty was overcome by diluting the sample until the acid concentration was below 0.02*N* and adding 5 ml. 1% potassium iodide solution to convert any free bromine in solution into iodine. This was then removed by careful addition of 0.02*N* sodium thiosulphate. The solution was then neutralized to thymolphthalein and the estimation completed as above.

In one experiment, as a check on the sulphite method, the formaldehyde content of an exhausted bath was estimated by the dimedone method [22]. There was complete agreement between the two methods.

Treated wools were analyzed for cystine and tyrosine content by the methods of Shinohara [17] and Lugg [13], respectively.

### *Test for Activation of Acid Bromate Solutions*

To determine if a substance activates an acid bromate solution, 0.1–0.2 g. of the substance was added to 10 ml. 5% $KBrO_3$ solution in 0.1*N* HCl, and the rate of liberation of bromine noted. There was no visible liberation of bromine from the acid bromate solution in 2 hr. at 20° C. in the absence of activators.

## Results

### *Treatment with Acid Bromate Solutions*

The treatment of wool with acid bromate solutions has been described in British Patent 614,271 [15], and some preliminary work was carried out on the lines of example one of this patent. In this example, the wool is treated at 25° C. with 4.85% $KBrO_3$ in 0.164*N* hydrochloric acid solution at a liquor ratio of 23:1. The effect of time of treatment is shown in Table I.

**TABLE I. Treatment of Wool with $KBrO_3$, According to British Patent 614,271**

| Time of treatment, min. | % $KBrO_3$ used up (on wt. of wool) | % Shrinkage |
|---|---|---|
| 0 | 0 | 30.0 |
| 15 | 1.35 | 17.8 |
| 30 | 1.80 | 6.4 |
| 45 | 2.25 | 2.9 |
| 60 | 2.50 | 1.9 |
| 90 | 3.45 | 2.5 |

It can be seen from these results that approximately 2.0–2.5% $KBrO_3$ on weight of wool is required to give complete unshrinkability. Potassium bromate is a comparatively expensive chemical, and as only about one half of the amount initially present is used up, the process becomes uneconomical unless worked on the standing bath principle. The high acid concentration used would, however, introduce plant corrosion problems. Attempts were made to reduce the initial amount of bromate to 2.5% but the time required for exhaustion was about 4 hr. This treatment time is excessive in view of the strong acid solutions used, and attempts were made to reduce this by varying the temperature and acid concentration. In all cases, exhaustion of 2.5% bromate onto the wool resulted in complete unshrinkability, but the conditions were always too severe for treatment times of 1 hr. or under to be practicable. The best conditions, as regards the properties of the treated wool, appeared to be 2½% bromate in 0.1*N* hydrochloric acid at 40° C. and liquor ratio 30:1 when the time of treatment was 2½ hr.

### *Properties of the Treated Wool*

The treated wool was a light yellowish-brown color, which could largely be removed by treatment with a dilute bisulphite solution. The alkali solubility of the wool was 14% when 2½% $KBrO_3$ was exhausted onto the wool, either by the method of British Patent 614,271 or using the conditions given above, compared with 10.5% for untreated wool. The loss in weight during treatment was approximately 2%. Microscopic examination showed that

50–55% of the fibers had the scale structure severely modified or destroyed.

*Mechanism of the Reaction*

It was found that a solution of bromic acid, prepared by addition of sulphuric acid to barium bromate solution, would only partially exhaust onto wool and no unshrinkability was produced even at pH 1. At this pH, potassium bromate in 0.1*N* hydrochloric acid solution exhausts more slowly than bromic acid, but the exhaustion is complete and unshrinkability is produced. The exhaustion of bromic acid onto wool is due to simple acid adsorption, in the same way that other strong acids, such as as hydrochloric and perchloric acids, are adsorbed, since 95% or more of the bromic acid removed from the solution could be recovered unchanged on shaking the wool with water. Hence it is very unlikely that there is any direct reaction between bromic acid and wool in reactions in which the wool becomes unshrinkable.

The addition of sodium chloride to hydrochloric acid solutions of $KBrO_3$ speeded up the reaction with wool considerably, whereas nitrate and perchlorate slowed down the reaction slightly. The results obtained using 4% $KBrO_3$ in 0.1*N* HCl at 35° C. and 60:1 liquor ratio, are given in Table II.

The accelerating effect of chloride ions on the reaction, together with the fact that bromic acid itself is only adsorbed by wool, suggests that in the normal reaction of $KBrO_3$ with wool in HCl solution the initial reaction is

$$2HBrO_3 + 10HCl \rightarrow Br_2 + 5Cl_2 + 6H_2O$$

The liberated chlorine and bromine then react with the wool to produce unshrinkability. It has been found [5] that in the reaction of wool with chlorine, very little of the chlorine combines with the wool, the majority being returned to the solution as chloride ions. A similar result has been observed for bromination in sulphuric acid solution, over 95% of the bromine being recovered as bromide.

Therefore, as the reaction proceeds, bromide will be formed and the slower bromate-chloride reaction will be partly superceded by the quicker bromate-bromide reaction.

$$HBrO_3 + 5HBr \rightarrow 3Br_2 + 3H_2O$$

**TABLE II. Effect of Neutral Salts on Bromate-Wool Reaction**

| Added salt | % in solution | Half-life, min. |
|---|---|---|
| None | — | 120 |
| Sodium chloride | 5 | 22 |
| | 20 | 4 |
| Potassium nitrate | 5 | 180 |
| Magnesium perchlorate | 5 | 180 |

## Activation of Acid Bromate Solutions

The time taken to liberate bromine from a bromate solution at pH 1 was used as a criterion for determining the degree of activation; liberation in under 2 min. was considered to be strong activation, in 2–10 min. as medium, and over 10 min. as weak or no activation. The results given in Table II are for

**TABLE III. Activation of Bromate Solutions at pH 1**

| Strong activation | Medium activation | Weak or no activation |
|---|---|---|
| Selenium dioxide | Hydrogen peroxide | Arsenious oxide |
| Sodium sulphide | Barium tri-thiocarbonate | Sodium dithionate |
| Sodium formaldehyde sulphoxylate | Potassium selenite | Sodium phosphite |
| | Hydrazine sulphate | Ammonium oxalate |
| Sodium hydrosulphite | Sodium hypophosphite | Benzaldehyde |
| Sodium sulphite | Paraldehyde | Chloral hydrate |
| Sodium meta-bisulphite | Methyl alcohol | Ethyl alcohol |
| Sodium thiosulphate | Iso-propyl alcohol | Iso-butyl alcohol |
| Stannous chloride | Ethylene glycol | Urea |
| Titanous chloride | Methyl oxalate | Acetamide |
| Ferrous sulphate | Lactic acid | Pyridine |
| Hydroxylamine sulphate | | Sucrose |
| Potassium nitrite | | |
| Ammonium thiocyanate | | |
| Formaldehyde | | |
| Glyoxal | | |
| Thiourea | | |
| Thioglycollic acid | | |

compounds partially or wholly soluble in 0.1*N* HCl and in the case of compounds showing medium or no activation represent a small selection of the compounds tried. Several insoluble compounds, particularly metals and metal sulphides, also showed some degree of activation.

The effect of compounds showing medium or strong activation on the reaction of wool with bromate in acid solution was next investigated. Varying amounts of the above compounds, up to 20% on the weight of wool, were added to a bath containing 4% $KBrO_3$ in 0.1*N* HCl at 40° C. and a 30:1 liquor ratio. Stannous and titanous chlorides were not investigated as they were hydrolyzed to basic salts or oxides in 0.1*N* HCl. The half-life of the reaction was determined in the usual way and compared with the half-life of the acid-bromate reaction. Activation of the bromate-wool reaction was shown by a reduced half-life without impairment of the unshrinkable properties of the treated wool. In several cases allowance had to be made for the presence of the oxidized form of the activator when determining the half-life, e.g., ferric iron in the case of ferrous sulphate. All of the compounds showing strong activation of bromate solutions activated the bromate-wool reaction, the half-life being reduced from 40 min. to 10–15 min. In addition, potassium selenite and hydrazine sulphate also speeded up the bromate-wool reaction. In the majority of cases small amounts only (0.5–2.0%) of activator were required, but in the case of formaldehyde and glyoxal about 10% was required.

Examination of the titration curves obtained in these activated reactions showed that they fell into one of three general types, as shown in Figure 1.

Table IV shows the division of the bromate activators into these three types.

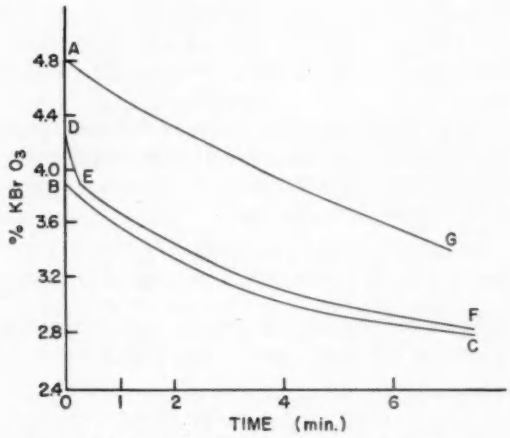


**Fig. 1.** Exhaustion of activated bromate solutions on to wool, showing the three types of curves obtained. (A-B-C; A-D-E-F; A-G). See Table IV and accompanying text.

Curves of types I and II suggest a two-stage process, and the most obvious explanation is that part of the bromate reacts quickly with the reducing agent to give bromide (A-B or A-D-E) and that the bromide formed then reacts more slowly with the unchanged bromate to give bromine, which then reacts with the wool (B-C and E-F).

Reactions which give a curve of type III presumably proceed by a different mechanism since the curve obtained is quite smooth. This differentiation is supported by the different amounts of activators required by types I and II compared with type III.

### *Mechanism of Reactions Involving Activators of Types I and II*

A study of the reaction of potassium bromate in 0.1*N* HCl with activators of types I and II was car-

**TABLE IV. Classification of Activators**

| Type I | Type II | Type III |
|---|---|---|
| Sodium sulphide | Sodium thiosulphate | Formaldehyde |
| Sodium nitrite | Hydrazine sulphate | Glyoxal |
| Sodium formaldehyde sulphoxylate | Hydroxylamine sulphate | |
| Sodium hydrosulphite | Potassium thiocyanate | |
| Sodium sulphite | Thiourea | |
| Sodium metabisulphite | Thioglycollic acid | |
| Potassium selenite | | |
| Selenium dioxide | | |
| Ferrous sulphate | | |

ried out initially in the absence of wool. An excess of bromate was reacted with a known weight of activator and the excess bromate determined in the usual way.

It was found that in the case of reducing agents containing sulphur or selenium, the reactions involved formation of sulphate or selenate, as previously reported [16, 21], e.g.,

$$4KBrO_3 + 3Na_2S \rightarrow 4KBr + 3Na_2SO_4$$
$$KBrO_3 + KCNS + H_2O \rightarrow KBr + KCN + H_2SO_4$$

In the case of thioglycollic acid, the results were less certain but the main reaction appeared to be

$$4KBrO_3 + 3HS{\cdot}CH_2COOH + 3H_2O \rightarrow 4KBr + 3HOCH_2COOH + 3H_2SO_4$$

Nitrite, hydrazine, and ferrous iron were oxidized to nitrate, nitrogen, and ferric iron, respectively, as previously reported [16, 21, 8], but hydroxylamine was found to be oxidized to nitric acid.

$$KBrO_3 + NH_2OH \rightarrow KBr + HNO_3 + H_2O$$

whereas Vitali [21] reported oxidation to nitrogen

$$4KBrO_3 + 12NH_2OH \rightarrow 4KBr + 18H_2O + 6N_2 + 3O_2$$

Reactions involving sulphide, formaldehyde-sulphoxylate, hydrosulphite, sulphite, selenite, nitrite, and ferrous iron were complete within 5 to 10 sec.; the other reactions required from 5 to 45 min. for completion.

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That the same reactions occur in the presence of wool was shown by reacting 6.8% $KBrO_3$ in 0.1*N* HCl, at 40° C. and a 30:1 liquor ratio, with sufficient reducing agent to produce a mixture of 4% $KBrO_3$ and 2% KBr. If the reduction of bromide was allowed to proceed completely before adding the wool, then except for three cases mentioned below, the half-lives of the reaction with wool were the same as for a mixture of 4% $KBrO_3$ and 2% KBr. If however the wool was added before the reducing agent, then the half-life depended on whether or not the reduction to bromide was immediate.

The half-lives of the reactions involving sulphite, metabisulphite and ferrous iron were greater than those of the other reducing agents. This was found to be due to the presence of relatively large amounts of sulphate ions in the solution (see Table XI).

*Optimum Conditions for Treating Wool with Bromate-Bromide and Bromate-Formaldehyde Mixtures*

The two types of reaction mixtures are considered together as this brings out more clearly the differences between them.

As in the case of simple acid bromate treatments, the quantity of bromate required to produce unshrinkability was found to be about 2.5%, on the weight of wool. Tables V to X show the effect of varying the treatment conditions on (*a*) the half-life of the reaction and (*b*) the % of the oxidizing power present as free halogen at the half-life. The concentration of bromate used was 4% in all cases, except for Table V.

From a practical point of view, a half-life of about 10 min. is desirable. From the results in Tables V to X, it is seen that the conditions necessary to

**TABLE V. Effect of Bromate Concentrations on Reaction in 0.1N HCl LR 30 : 1 at 40° C. Using 2% KBr or 10% HCHO**

| % $KBrO_3$ | Bromide reaction | | Formaldehyde reaction | |
|---|---|---|---|---|
| | Half-life, min. | % free halogen | Half-life, min. | % free halogen |
| 1 | 9 | 0.8 | 7 | 0.9 |
| 4 | 10.5 | 5.0 | 4.5 | 2.3 |

**TABLE VI. Effect of Bromide Concentration on Reaction in 0.1N HCl LR 30 : 1 at 40° C.**

| % KBr | Half-life, min. | % free halogen |
|---|---|---|
| 0 | 40 | 0.3 |
| 0.5 | 23 | 1.2 |
| 1.0 | 15.5 | 3.0 |
| 2.0 | 10.5 | 5.0 |
| 4.0 | 6 | 7.0 |

**TABLE VII. Effect of Formaldehyde Concentration on Reaction in 0.1N HCl LR 30 : 1 at 35° C.**

| % HCHO | Half-life, min. | % free halogen |
|---|---|---|
| 0 | 105 | — |
| 2 | 30 | 0.2 |
| 5 | 15 | 0.5 |
| 10 | 7.5 | 2.0 |
| 20 | 4 | 3.1 |
| 50 | 2.5 | 8.3 |

**TABLE VIII. Effect of HCl Concentration on Reaction with 2% KBr or 10% HCHO at 40° C. and LR 30 : 1**

| HCl concentration | Bromide reaction | | Formaldehyde reaction | |
|---|---|---|---|---|
| | Half-life, min. | % free halogen | Half-life, min. | % free halogen |
| 0.20*N* | 2.5 | 29.5 | 2 | 24.6 |
| 0.10*N* | 10.5 | 5.0 | 4.5 | 2.3 |
| 0.05*N* | 33 | 0.3 | 8 | 0.4 |
| 0.02*N* | Bromate absorbed—no unshrinkability | | 35 | 0.2 |

**TABLE IX. Effect of Liquor Ratio on Reaction with 2% KBr or 10% HCHO in 0.1*N* HCl at 40° C.**

| Liquor ratio | Bromide reaction | | Formaldehyde reaction | |
|---|---|---|---|---|
| | Half-life, min. | % free halogen | Half-life, min. | % free halogen |
| 20 : 1 | 8 | 3.1 | 3 | 2.0 |
| 30 : 1 | 10.5 | 5.0 | 4.5 | 2.3 |
| 40 : 1 | 12.5 | — | 6.5 | — |
| 60 : 1 | 14 | 8.5 | 8 | — |
| 100 : 1 | 14.5 | — | 14 | 2.0 |

**TABLE X. Effect of Temperature on Reaction with 2% KBr or 10% HCHO in 0.1*N* HCl and LR 30 : 1**

| Temperature, °C. | Bromide reaction | | Formaldehyde reaction | |
|---|---|---|---|---|
| | Half-life, min. | % free halogen | Half-life, min. | % free halogen |
| 20 | 65 | 0.4 | 40 | 1.0 |
| 30 | 23 | 2.9 | 11 | — |
| 35 | 15 | — | 7.5 | 2.0 |
| 40 | 10.5 | 5.0 | 4.5 | 2.3 |
| 45 | 6 | — | — | — |

achieve this are 2% KBr on weight of wool in 0.1*N* HCl at 40° C. for the bromide reaction or 5–10% formaldehyde in 0.1*N* HCl at 30°–35° C. for the formaldehyde reaction. In both cases the liquor ratio is 30:1 and the bromate concentration about 2.5%, according to the degree of treatment required.

*Properties of the Treated Wool*

The wool treated by the bromate-bromide method was slightly discolored, but this was removed by treatment with a dilute bisulphite solution. The alkali solubility of wool treated under the optimum conditions was 16.0%, that of untreated wool being 9.8%. Microscopic examination showed that some 70% of the fibers had the scale structure severely modified or destroyed.

The wool treated by the bromate-formaldehyde method was of a good color, and the residual oxidizing power, as estimated by the staining produced with acidified KI solutions, was very low and it is probably unnecessary to aftertreat with an antichlor, such as bisulphite. The alkali solubility of the treated wool is lower than that usually found for an antishrink treatment of this type. In the case of treatment with 2½% $KBrO_3$ and 10% HCHO in 0.1*N* HCl, the alkali solubility is 12.2%, and in 0.05*N* HCl it is 10.2%. This suggests that during the reaction, some of the formaldehyde reacts with the wool to form new cross-links. This is supported by the fact that wool treated under similar conditions without the bromate has an alkali solubility of 7.6%.

The microscopic appearance of the fibers also suggests less damage than with the other bromate reactions; some 40% of the fibers had the scale structure severely modified or destroyed.

*Mechanism of the Bromate-Formaldehyde-Wool Reaction*

From the results in the preceding section, it can be seen that the bromate-formaldehyde-wool reaction differs in many respects from the bromate-bromide-wool reaction.

*a.* The effect of bromate concentration on the half-life of the reaction is reversed (Table V).

*b.* The bromate-formaldehyde reaction proceeds in 0.02*N* HCl at 40° C., whereas the bromate-bromide reaction does not (Table VIII). In the experiments summarized above, the wool was wet out in aqueous Dispersol VL. The effect of wetting out the wool in Dispersol VL in 0.02*N* HCl before reaction with bromate in 0.02*N* HCl, failed to induce the bromate-bromide reaction to proceed (apart from adsorption), whereas in the case of the bromate-formaldehyde reaction the half-life was reduced from 35 to 20 min.

*c.* Changing the liquor ratio from 20:1 to 100:1 has a greater effect on the half-life of the formaldehyde reaction than on that of the bromide reaction (Table IX).

*d.* In general the amount of free halogen in solution for a given half-life is greater for bromate-bromide reactions than for ones involving bromate

**TABLE XI. Effect of Neutral Salts on Bromate-Bromide and Bromate-Formaldehyde Reactions**

| Added salt | % in solution | pH of solution | Half-life, min. Bromide reaction | Half-life, min. HCHO reaction |
|---|---|---|---|---|
| None | — | 1.06 | 14 | 14 |
| Sodium chloride | 5 | 1.04 | 7 | 11.5 |
| | 20 | 1.14 | 3 | 3 |
| Potassium nitrate | 5 | 1.15 | 27 | 18 |
| | 20 | 1.00 | 28 | 21 |
| Magnesium perchlorate | 5 | 1.19 | 37 | 21 |
| | 20 | 1.03 | 38 | 22 |
| Sodium sulphate | 0.167 | 1.08 | 20 | 15.5 |
| | 0.33 | 1.06 | 27.5 | 23 |
| | 0.83 | 1.20 | 58 | 30 |
| | 5 | 1.67 | No reaction | 150 |
| | 20 | 1.81 | No reaction | 150 |

and formaldehyde. This is probably due to reaction between formaldehyde and free bromine.

$$HCHO + Br_2 + H_2O \rightarrow HCOOH + 2HBr$$

This is supported by the fact that in the absence of wool, the bromate-formaldehyde bath exhausts more quickly than in its presence.

It was also found that addition of neutral salts, particularly sulphates, to the two reactions had a greater effect on the bromide reaction than on the formaldehyde reaction. This is shown in Table XI which is for reaction with 4% $KBrO_3$ in 0.01*N* HCl at a 60:1 liquor ratio and 35°C., with either 2% KBr or 10% HCHO.

These facts indicate that the mechanism of the formaldehyde-activated bromate reaction is different from that of the other reducing agents.

Analyses of formaldehyde-bromate solutions for total oxidizing power, bromate oxidizing power, formaldehyde and total acidity both in the presence and absence of wool were inconclusive, from 0.5 to 2.0 mols. formaldehyde per mol. bromate being used up.

That the reaction did not involve the intermediate formation of bromide was shown by carrying out the wool reaction in 0.1*N* $H_2SO_4$ in the presence of 2% silver sulphate. A very slight precipitate of silver halide was formed, but the speed of the reaction, the free halogen in solution, and the shrinkage results were identical with those obtained in the absence of silver sulphate. Similar results were obtained in 0.1*N* $HNO_3$ solution using 2% silver nitrate.

This suggests that the reaction involves reduction of the bromate to bromine or hypobromite, without intermediate formation of bromide. A less likely explanation would involve the formation of a bromite.

*Reaction of Wool with Glyoxal-Bromate Solutions*

This reaction has not been studied to any extent, but the results obtained suggest that the same type of reaction is involved as in the case of formaldehyde-bromate mixtures. Glyoxal is a di-aldehyde, and in general smaller amounts are required to activate bromate solutions than are necessary in the corresponding formaldehyde reactions.

*Reactivity of Bromate Solutions with Amino Acids Present in Wool*

Determination of the cystine and tyrosine contents of bromate-treated wools showed that both amino acids had been attacked which is in agreement with previous work [3]. The results obtained are given in Table XII.

**TABLE XII. Amino Acid Contents of Treated Wools**

| Treatment | % Cystine | % Tyrosine |
|---|---|---|
| 2½% $KBrO_3$ in 0.1*N* HCl at 40° C. | 10.9 | 5.1 |
| As above + 10% HCHO | 10.5 | 4.95 |
| Untreated wool | 12.0 | 5.35 |

In addition, solutions of potassium bromate in 0.1*N* HCl reacted with the amino acids methionine, tryp-

tophane, and histidine in addition to cystine and tyrosine. Similar results were obtained in the presence of formaldehyde.

## Summary and Conclusions

The activation of acid bromate solutions has been studied and the activating agents divided into two classes. The mechanism of the reactions taking place with activating agents other than aldehydes has been shown to consist of a preliminary reduction of bromate to bromide, followed by a bromate-bromide-acid reaction to produce bromine. In the case of activation by aldehydes, the intermediate formation of bromide appears unlikely, since the reaction is unaffected by addition of moderate amounts of silver salts.

Of the two types of activated processes, the one using formaldehyde possesses several advantages over those involving intermediate formation of bromide. There is less damage, as shown by the alkali solubility test, and as there is less free halogen present in the solution during the reaction, the treatment should produce very level results.

Analysis of treated wools has shown that, in common with other oxidative processes in which unshrinkability is produced without excessive degradation, both cystine and tyrosine residues in the wool are attacked.

## Acknowledgments

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The activated bromate processes described in this paper are covered by British Letters Patent Nos. 723,559, 723,560 and 723,561, the property of Precision Processes (Textiles) Limited.

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# The Cellulose-Alkali Hydroxide-Water System in the Cyanoethylation of Cotton Cellulose

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**Abstract**

When cotton cellulose is cyanoethylated with a large excess of acrylonitrile in the presence of aqueous alkali hydroxides at a fixed time and temperature, the rate of reaction is controlled by the ratios of base:cellulose:water. The variations in yield and rate of cyanoethylation can be explained by considering the changes brought about in cellulosate ion concentration, solubility of acrylonitrile, and bond strengths, by varying the amount, concentration, and nature of the alkali hydroxide on the cellulose. The microbiological resistance of the product is dependent on the same ratios because of the formation of carboxyl groups in the product, the rate of which formation is governed by the strength and quantity of the aqueous base, and the time of the reaction.

The rate of reaction and yield of cyanoethylated cotton can be greatly improved by the inclusion of hydrotropic salts in the padding liquor.

As part of a program to elucidate the mechanism and effect of catalysts in the etherification reactions of cotton cellulose, this laboratory has studied the cyanoethylation reaction between cotton cellulose and acrylonitrile [1, 3]. In a previous publication [9], it was shown that in the presence of a large excess of acrylonitrile this reaction is dependent on the ratio NaOH:cellulose:$H_2O$, and that isologous nitrogen curves can be drawn on a ternary diagram to conveniently represent the extent of reaction as a function of these three variables.

In order to gain further insight into the mechanism of this reaction, similar series of experiments were carried out utilizing LiOH, KOH, and CsOH.

The experimental techniques used were essentially the same as reported previously [9]. All the alkali bases were reagent grade.

## Results

The isologous nitrogen curves are represented in Figure 1 which shows the composition areas in which maximum yields are obtained for the bases studied, and the pattern followed by decreasing nitrogen content lines. For convenience, only a portion of the total pattern for each base is plotted. The figure indicates that the areas for maximum reaction in the series LiOH—NaOH—KOH decrease in base and water content. The optimum area for CsOH is at a higher base concentration, but at a lower water content. The figure also shows that while the position of maximum nitrogen varies, the value of the nitrogen content achieved at each optimum ratio increases steadily from LiOH to CsOH.

Figure 2 shows the variation of nitrogen content of the product with time, utilizing the optimum ratios of base:cellulose:water in the cyanoethylation mixture. It is apparent that after 30 min. at 60° C. the reaction is reaching equilibrium conditions. Longer time values were not considered since these would have little benefit in determining the relative efficacy of the bases as catalysts. They would introduce undesirable complications in the way of subsequent side reactions, for example, the alkaline hydrolysis of the nitrile group to the carboxyl group. The anomalous yield obtained with CsOH after 15 min. of reaction is attributed to this hydrolysis.

Figure 3 shows the areas of optimum yield for the bases in terms of mole ratios. For convenience only a portion of the ternary diagram is depicted. A line originating at the water apex and drawn through the center of each area will terminate on a line connecting the base and cellulose apices. From this intersection the mole ratios of base to cellulose may be determined for the optimum concentrations. For LiOH this base:cellulose ratio is 1.4, for NaOH, it

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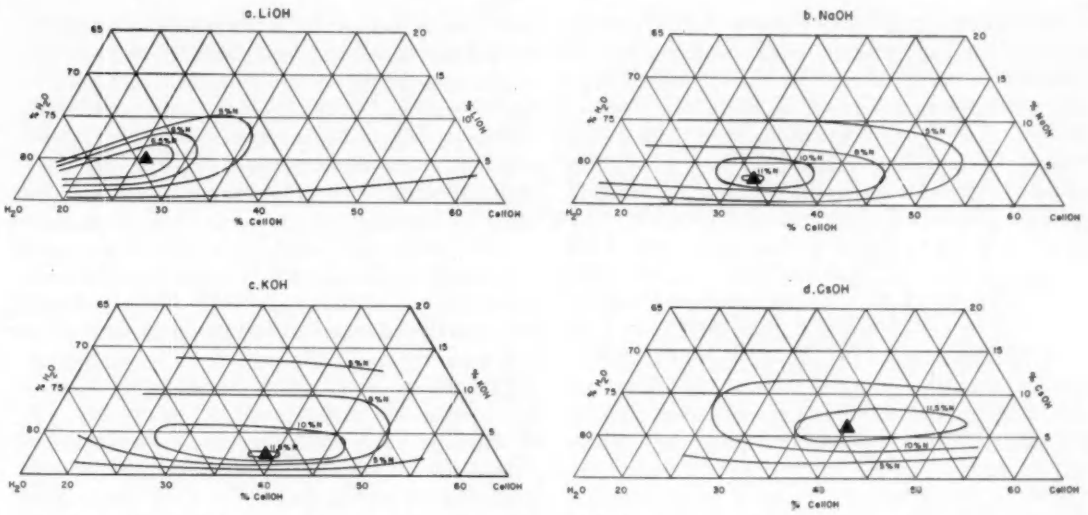


**Fig. 1.** Nitrogen contents of cotton types cyanoethylated for 30 min. in the presence of aqueous lithium, sodium, potassium and cesium hydroxides. The solid triangles denote the optimum ratios for maximum rate and degree of substitution at 60° C. with a 50:1 acrylonitrile: cellulose ratio.

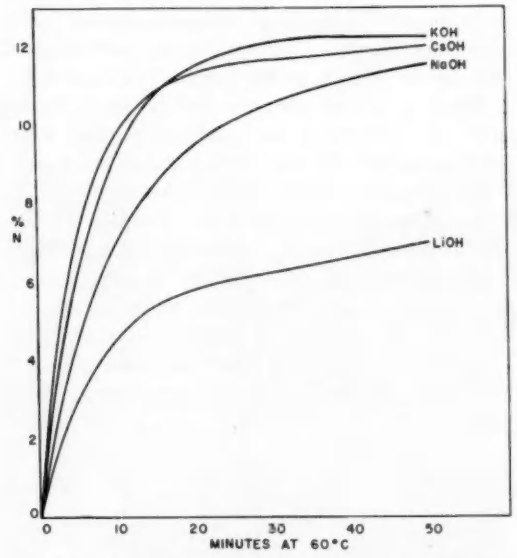


**Fig. 2.** Rates of cyanoethylation of cotton tapes with optimum quantities of lithium, sodium, potassium, and cesium hydroxides.

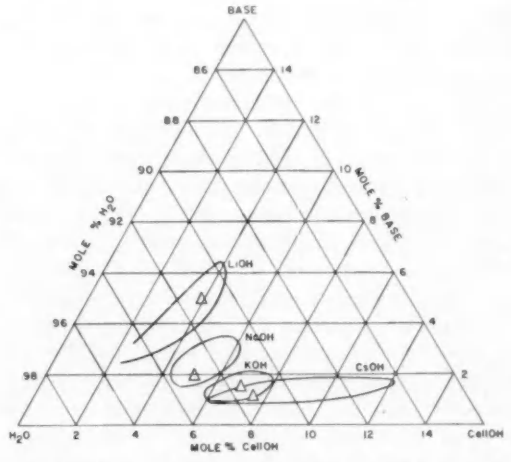


**Fig. 3.** Optimum mole ratios of base: cellulose: water in the cyanoethylation of cotton tapes at 60° C. in the presence of aqueous lithium, sodium, potassium, and cesium hydroxides. The areas shown represent limits of 6.5%, 10.0%, 11.0%, and 11.5% nitrogen for the lithium, sodium, potassium, and cesium hydroxides, respectively.

is 0.4, for KOH it is 0.2, and for CsOH it is 0.15. No theoretical deductions could be made from this, however, since the diagram clearly indicates that at these base:cellulose ratios the boundary conditions are determined by the water content of the system. The symmetry of the areas about these fixed base: cellulose ratio lines is further evidence that while certain base:cellulose ratios are desirable, the advantage to be gained by maintaining these ratios is limited by the total water present in the system.

No relationship could be found between the base: cellulose ratio at optimum yield conditions and the swelling power of the various bases. Therefore, it was concluded that the swelling of the fibers cannot be considered to be the governing phenomena in this reaction, except that it determines the diffusability of the liquid phase during the course of the reaction. This swelling depends also, of course, on fabric structure. Evidence of this is the increasing value of the nitrogen content at optimum ratios in the order LiOH—NaOH—KOH—CsOH, while the swelling power of the bases decreases in the same order [7].

In a previous paper [9], it was stated that during the cyanoethylation reaction some of the CN groups are hydrolyzed to COOH. In the presence of the aqueous alkali these carboxyethyl groups bring about intense swelling of the cellulose with attendant decrease in crystallinity or increase in accessibility. This increase in chemical accesibility requires higher cyanoethyl substitution to protect the exposed anhydroglucose units from microbiological attack. The loss of resistance to microbiological attack is not merely a function of the original swelling of the cellulose, but is also dependent on the carboxyethyl content of the product.

In this connection it is interesting to note that cyanoethylation of cotton tape to 3.5% N, using the optimum ratio of cellulose:base:water gave the lowest carboxyethyl:cyanoethyl ratio obtained in any sample having this nitrogen content. This sample was produced in minimum time, and even though 10% sodium hydroxide was used as the padding liquor, the sample had excellent soil burial resistance.

In samples containing the various alkali bases at the same hydroxide ion activity, it is found that the nitrogen yield increases from lithium through cesium. Since the ionization of the cellulose must be equal at equal hydroxide ion activities in the aqueous phase, this variation in yield must be dependent on the nature of the alkali cation. It is difficult to ascertain whether this variation in cation nature exerts its effect by a change in the strength of the cellulosate-cation ion-pair bond, by a change in the solubility of the acrylonitrile in the aqueous phase, or both. The same charge and size properties of the cation which determine its properties in the ion-pair bond also determine its "salting out" properties in the aqueous phase [2].

In order to understand these effects better, it became desirable to determine the solubility of acrylonitrile in aqueous bases [5]. These data indicated that at the same alkali hydroxide molality, the solubility of the acrylonitrile increases in the order LiOH—NaOH—KOH—CsOH. This increase in solubility of the acrylonitrile in the aqueous base is in the same order as the increasing nitrogen yields obtainable at the optimum base:cellulose:water ratio for each alkali hydroxide.

This "salting out" effect can also be demonstrated by adding NaCl to aqueous base padding solutions; increasing concentrations of NaCl at any particular base concentration lead to decreasing nitrogen values in the product.

The reverse effect can be demonstrated through the use of the phenomenon of hydrotropy [6]. Hydrotropic salts which increase the solubility of acrylonitrile in the aqueous phase also increase the cyanoethylation yield and rate. Salts which have proved capable of exerting this effect include sodium iodide, potassium iodide, sodium benzoate, sodium salicylate, and sodium xylenesulfonate. Several of these salts have also been reported [8] by the Stamford Research Laboratory of American Cyanamid Co. to improve the cyanoethylation reaction with cotton and to reduce the formation of side products.

Table I illustrates the effect of a typical hydrotropic salt included in the padding mixture. The control samples were padded with a 2.3% solution of NaOH to a 75% wet pickup; the samples with KI were padded with a 2.3% solution of NaOH with KI added to make a 25% KI solution based on the water and KI. The pickup of these samples was adjusted so as to compensate for the extra mass due to the KI; analysis of duplicate samples prior to reaction showed that the base:cellulose:water ratio was essentially constant for all samples in both series.

**TABLE I**

| Time of reaction, min. | Per cent nitrogen in product* | |
|---|---|---|
| | 2.3% NaOH | 2.3% NaOH, 25% KI |
| 5 | 1.5 | 1.8 |
| 10 | 2.2 | 3.2 |
| 15 | 2.6 | 4.1 |
| 20 | 2.7 | 5.6 |
| 30 | 3.1 | 7.8 |
| 40 | 3.1 | 8.7 |

* Padding solution

## Discussion

In order to explain the sequence of the reaction steps and their variations, the cotton cellulose is pictured as a hydrophilic polymer solvated and surrounded by a sheath of aqueous base; it is swollen to varying degrees, and its hydroxyl groups are ionized to varying concentrations of cellulosate ion, depending on the activity of the hydroxide ions in the aqueous phase.

The cyanoethylation reaction is assumed to take place between the cellulosate-alkali ion-pair and the acrylonitrile dissolved in the aqueous phase. The rate and extent of reaction will then depend on the concentration of the cellulosate ion—and thereby on the base strength—on the concentration of acrylonitrile in the aqueous phase, and on the strength of the cellulosate-cation ion-pair bond. All other conditions being equal, the latter will determine the rate of the reaction, since it is assumed that the greater attraction between the unshared electron pair on the electronegative cellulosate oxygen atom and the electropositive terminal carbon atom of acrylonitrile is the driving force for this reaction.

The cotton cellulose must preferentially absorb sufficient alkali hydroxide and water from the padding solution to form a maximum concentration of cellulosate ions. The base:cellulose:water ratio at this pickup will be determined by the concentration of the padding solution, the fabric structure, and by the nature of the base. If any excess base is present over that amount required for cellulosate ion formation, it serves to "salt out" the acrylonitrile. In the calculation of the optimum amounts of reagent present, consideration must be given to the amount of water in the acrylonitrile, since this will enter into the equilibrium between cellulose, soda-cellulose, and aqueous base. The acrylonitrile:cellulose mass ratio influences the course of the reaction because the water in the acrylonitrile participates in the three-phase equilibria with aqueous base.

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# INDUSTRIAL SECTION

## Modified Acid Colloid Process for Controlling Wool Fabric Shrinkage

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**Abstract**

The influences of several process variables on the dimensional stabilization of wool fabrics with melamine resin acid colloid were studied in the laboratory. Preparation of acid colloid, different organic acids, curing temperature, and solids deposited were among the variables examined. It was found that low temperature curing with higher resin solids deposits is as effective as high temperature curing with lower solids in controlling wash shrinkage.

THE stabilization of wool fabrics with melamine formaldehyde resins has been known for more than a decade, and considerable patent literature has accumulated[2–8].

The earliest treatments involved the application of melamine formaldehyde precondensates in essentially monomeric form and a subsequent high temperature cure (300° F.). This treatment gave shrinkage control but imparted a stiff hand to the fabric and yellowed it appreciably. Because wool is a good thermal insulant, long curing cycles were needed to effect adequate heat penetration.

The later discovery of melamine acid colloid [9] led to an improved wool stabilization process [2, 3, 7]. By this process somewhat lower temperatures of cure (260° F.) were possible, but the outstanding result was a notable increase in the softness of hand in the stabilized goods over that which can be obtained with regular melamine formaldehyde.

Experimental work in our laboratory has yielded some further refinements of the wool stabilization process which are of practical importance. The present finding is that stabilization of wool with soft hand can be achieved by simple drying of the goods, even by air drying, after the melamine acid colloid has been applied. Since this process requires only drying equipment which is in place in many mills, a study of some of the process variables should be of wide interest. Such a study is reported in this paper.

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### Experimental Work

*Materials and Methods*

*Melamine resin acid colloid.* Acid colloids used for wool shrinkage reduction are formed by mixing a relatively large amount of acid, usually of the organic type, with an aqueous solution of methylated methylol melamine. Upon standing for several hours at room temperature, this mixture, at first water-white, develops a blue haze of colloidally suspended partially polymerized resin.

The preparation procedure used throughout this work was as follows: 140 g. by weight of Resloom [2] M-75 was diluted at room temperature with 480 g. of water. One mole of the organic acid was then

[2] Monsanto trade mark. Resloom M-75 contains 60% by weight of metiylated methylol melamine.

made up to 204 g. with water and stirred into the diluted Resloom. This mixture, containing 10% Resloom solids, was then heated to 120° F. and allowed to stand for 16 hr. at room temperature. Thereafter it was further diluted with water so that it would deposit the desired amount of Resloom solids when test specimens of fabric were padded through it. Wet pickups were about 85%. For example, the standard acetic colloid was made by diluting 140 parts of Resloom M-75 with 480 parts of water, and then adding a solution which consisted of 61 parts of glacial acetic acid in 143 parts of water. After being heated to 120° F. and aged for 16 hr., this colloid was diluted to 6% resin solids with an additional 550 parts of water. Padded on the fabric at 85% pickup, the final solution deposited about 5% resin solids.

Heating of the melamine resin–organic acid mixture to 120° F. prior to the 16-hr. aging prevented gelling of the colloid. In some cases, particularly for glycolic acid, clear gels would often form rather than blue colloids if the heating were omitted. This gelling was shown to be caused by use of too cool solutions.

The aging period of 16 hr. was mainly a convenience which permitted overnight holding of the solutions for use the next day. A preliminary study of the effects of colloid aging showed that no aging gave finished fabrics with a stiff hand and that stiffness of finish decreased with age of colloid up to about 5 hr. Thereafter aging had little effect on hand. Degree of stabilization was approximately the same regardless of age of colloid.

The study was made with laboratory equipment and facilities only. The general procedure consisted of cutting out wool fabric samples approximately 16×24 in. and marking them suitably for subsequent framing and for shrinkage measurements. These samples were wetted out in the acid colloid solution, passed between squeeze rolls, framed to original dimensions on pin frames, dried for 10 min. at 200° F. in a forced circulation air oven, and further cured on frames where such curing was necessary.

The wool fabric used in all experiments was a dyed all wool flannel. All samples were taken from the same roll of goods.

Relaxation and shrinkage were determined by Tentative Test Method 41–52 of AATCC [1]. In this procedure relaxation is obtained by wetting the specimen with a spray of water, hydroextracting, and pressing on a flat bed without tension. Felting shrinkage is determined by washing the test specimens for 75 min. in a rotary washer at 100° F. with 0.1% soap and following with two 5-min. clear water rinses. The washed samples are hydroextracted, pressed on a flat bed and measured. Total shrinkage less relaxation gives felting shrinkage. While warp and filling shrinkage were determined separately, the algebraic sum of them is reported as area shrinkage in this paper. This is done for simplification.

### Reliability of Shrinkage Data

In this study the final relaxation and wash shrinkages are the sole means by which the influence of changes in process variables can be measured. However, such shrinkage measurements, made at the end of a series of processing operations, contain accumulated errors. The reliability of single observations was not known. Accordingly, an experiment was conducted to provide this information.

Three samples of the wool fabric were wet out in parallel in the same acetic acid colloid bath. This colloid contained 6% melamine resin solids and was made by the method already described. The wet samples were then padded, dried, cured, and washed in parallel. The cure consisted of 10 min. at 250° F.

The shrinkage data that emanated from these tests are shown in Table I, together with the averages of the three values. It can be seen that single observations vary considerably even under the parallel conditions of this experiment and that little significance can be attached to differences of 1% or less in single observations.

**TABLE I. Variation in Shrinkage of Similar Wool Samples Processed Simultaneously**

| | Area shrinkage, % | | | |
|---|---|---|---|---|
| | Sample 1 | Sample 2 | Sample 3 | Avg. of 3 |
| Relaxation | 0.6 | 1.7 | 1.7 | 1.3 |
| Felting, 1 wash | 3.8 | 4.1 | 3.7 | 3.9 |
| Felting, 3 washes | 6.7 | 6.8 | 5.7 | 6.4 |

5% melamine acetic acid colloid solids applied. Samples cured 10 min. at 250° F.

### Effects of Curing and Aging

In some of the early experiments of this investigation there were indications that aging of the treated fabric prior to washing gave an improvement in

shrinkage control. The data, however, were not consistent, and after some of the other process variables had been examined, the experiment was repeated under more complete control.

Nine test specimens of the wool fabric were impregnated simultaneously in the same acetic colloid bath and then padded so as to deposit 5% melamine resin solids. All of the samples were dried for 10 min. at 200° F. Three were immediately subjected to relaxation, three others were given an additional cure of 10 min. at 250° F. and then relaxed, and the remaining three were aged for 24 hr. at room temperature and relaxed. For each of these sets the first wash was made directly after the relaxation, but thereafter the samples were again grouped and received the second and third washes simultaneously.

The shrinkage data from this series are shown in Table II as averages for the parallel triplicates. These data reveal that (*a*) all of the treatments effect a sharp reduction in shrinkage from the untreated control, (*b*) that the additional cure at 250° F. may give a further small reduction in shrinkage, and (*c*) that aging has, if anything, a detrimental effect on shrinkage. These observations support the conclusion that aging of samples between the drying and washing has no particular value.

**TABLE II. Influence of Curing and Aging on Wool Shrinkage**

| Curing | Aging | Average (3) area shrinkage, % Relaxation | Felting 1 wash | Felting 3 washes |
|---|---|---|---|---|
| Control, untreated | — | 7.5 | 17.2 | 30.0 |
| 10 min., 250° F. | None | 1.3 | 3.9 | 6.4 |
| 10 min., 200° F. | None | 1.2 | 4.4 | 7.3 |
| 10 min., 200° F. | 24 hr. | 2.3 | 4.0 | 8.1 |

5% melamine acetic acid colloid solids applied.

## Effects of Kind and Amount of Acid

Acetic acid used in forming the melamine acid colloids for the above described experiments is volatile. Even though wool itself might hold acetic against the high drying and curing temperatures, it seemed possible that some of the less volatile organic acids might be retained through the process to a higher degree and give better performance than acetic. It was also possible that changes in the amounts of acid used to form the colloids might alter the results.

Accordingly, colloids were formed with four different organic acids including acetic. These acids were used on an equimolar basis with each other rather than on an equal weight basis. Also, in two cases colloids were formed with double the molar quantities of acid for the purpose of revealing effects due to concentration. These colloids were applied so as to deposit 5% melamine resin solids on the wool. The samples were then dried in parallel at 200° F., aged in parallel for 24 hr., and finally given relaxation and washings simultaneously.

The shrinkage data for the various acids and the different acid concentrations are presented in Table III. In this table the term "mole" is relative, not absolute, in that 1 mole of acid represents the concentration of acetic used in the preparation of the standard acid colloid. The shrinkage values are for single samples.

**TABLE III. Effects of Kind and Amount of Acid in Colloid on Wool Shrinkage**

| Acid and relative amount | Area shrinkage, % Relaxation | Felting 1 wash | Felting 3 washes |
|---|---|---|---|
| Acetic, 1 mole | 3.5 | 5.8 | 11.5 |
| Acetic, 2 moles | 2.4 | 6.2 | 10.8 |
| Glycolic, 1 mole | 1.7 | 5.2 | 9.6 |
| Glycolic, 2 moles | 3.2 | 4.0 | 8.2 |
| Gluconic, 1 mole | 3.5 | 4.7 | 9.1 |
| Lactic, 1 mole | 2.8 | 6.0 | 11.2 |
| No treatment | 8.0 | 17.0 | 28.9 |

5% melamine acid colloid solids applied. Cured 10 min. at 200° F., aged 24 hr.

The data show some variability as might be expected. In general, it appears that glycolic and gluconic acids give slightly better shrinkage reduction than the other acids, although all of the acids are surprisingly similar in performance. It also seems to be a fact that doubling of acid concentration has little effect on shrinkage. The conclusion therefore is warranted that volatility of the acid is not a major factor in the process. Furthermore, excesses of acid do not seem to be either detrimental or beneficial to shrinkage.

## Effect of Amount of Resin

All of the foregoing tests were made at 5% of melamine resin solids on the dry weight of the fabric. To develop information along this line, a study of the effects of variation in resin solids on shrinkage was

undertaken. In this endeavor all other process variables were held as nearly constant as reasonable care would permit.

The execution of this experiment was as follows: a large batch of standard melamine acetic acid colloid was made up, and portions of it were diluted varying amounts. The dilutions were made so that impregnation and padding of the wool samples would yield melamine resin solids add-ons ranging from 2 to 10%. Two samples were treated with each dilution and both were dried for 10 min at 200° F. One of each of these pairs was subsequently given an additional cure of 10 min. at 250° F. The samples were thereafter grouped together and put through the regular relaxation and washing operations.

The felting shrinkages as a function of melamine resin solids applied are plotted in Figure 1. These curves clearly reveal that shrinkage decreases with increasing resin solids, sharply at low concentration and then more slowly at the higher resin add-ons. Again it is evident that the additional 250° F. cure consistently gives better shrinkage control than simple 200° F. drying. This difference appears to be somewhat larger after 3 washes than after 1 wash.

Shrinkage values taken from Figure 1 are replotted as a function of number of washes in Figure 2. The curves show that at high resin add-ons there is far less progressive shrinkage than at lower add-ons. Again, the curves indicate the slight superiority of 250° F. curing over simple 200° F. drying.

Finally, an interesting comparison of simple 200° F. drying with the 250° F. additional cure is presented in Figure 3. For the construction of this graph, amounts of melamine resin necessary to give the same shrinkage by these two treatments were selected from Figure 1. These selections were made over the whole range of applied solids for both 1 and 3 washes.

The plot yields a straight line. That is, a direct proportionality exists between simple 200° F. drying and the 250° F. additional cure. The interpretation of this proportionality is quite obvious. It means that 1.5 parts of melamine resin solids applied by the simple 200° F. drying process produce exactly the same shrinkage control as does 1 part of melamine resin solids with the additional 250° F. cure. In other words, a 50% increase in resin solids add-on can be substituted for the extra heating.

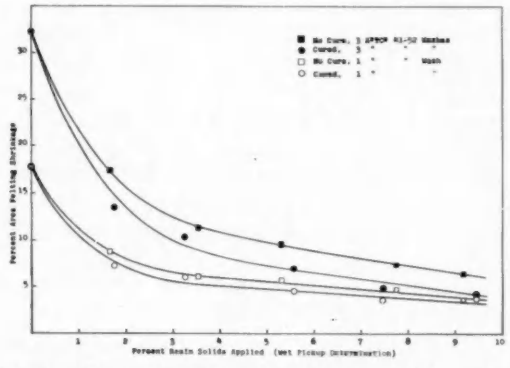


**Fig. 1.** Effects of varying resin add-ons and different heat curves on felting shrinkage.

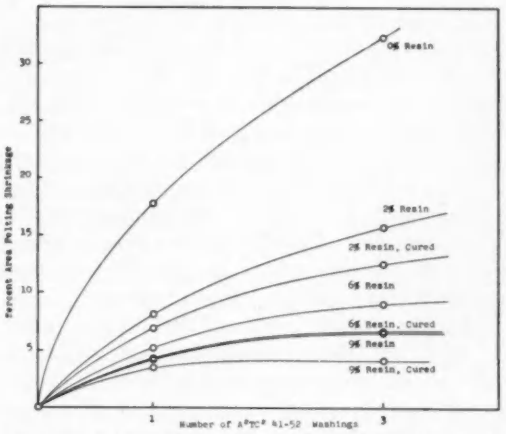


**Fig. 2.** Felting shrinkage for varying resin add-ons and two different curves as a function of washings.

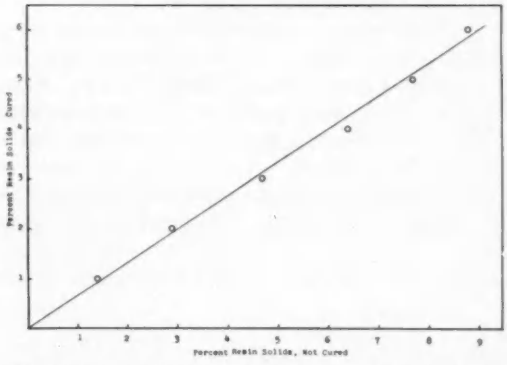


**Fig. 3.** Resin add-ons with 250° F. cure as a function of resin add-ons with 200° F. drying for equal felting shrinkages.

## Discussion

A few experiments were conducted at drying temperatures between 200° and 250° F., as well as at room temperature. A drying temperature of 225° F. probably gives slightly better shrinkage control than 200° F. Mere drying of acid colloid-impregnated wool at room temperature produces excellent shrinkage reduction. Aging of colloid-impregnated fabric in the wet condition at room temperature gave no shrinkage control.

While fabric shrinkage is the main concern of this paper, there are two other fabric properties that deserve mention, namely, hand and color. Little, if any, firming up of the cloth occurs where acid colloid is used and where processing temperatures are below 260° F.

The color of wool fabric is altered by elevated temperatures, whether or not melamine resin is present. This discoloration increases in intensity with both time and temperature of exposure. The heat discoloration is easily recognized as a yellowing of white goods. Where goods are already colored, the yellowing may appear as a change in shade. It was observed in the present work that samples cured at 250° F. were distinctly yellower than those processed at 200° F. However, after multiple 41–52 washes, this discoloration had largely disappeared.

It has already been mentioned that the same fabric was used throughout this investigation. Different fabrics would undoubtedly differ in degree of shrinkage and in resin add-on requirements for shrinkages equal to those shown in the foregoing tables and graphs. However, any study of the effects of fabric construction and of different wools on shrinkage was beyond the scope of this work.

The low-temperature stabilizing process for wool fabric in a very simple one. High temperature curing equipment is not needed. By adjustment of the melamine resin solids applied to fabric, any desired degree of shrinkage control within reason apparently can be produced.

It does seem that some reason should be used in controlling wool shrinkage. The degree of shrinkage control sought should be dictated by the end-use requirements of the fabric. For example, a small resin add-on to all-wool suiting should be enough to prevent the progressive small shrinkage that often occurs during the life of the garment. On the other hand, a shirting needs a relatively large resin add-on to stabilize it through multiple washes.

The low-temperature stabilization process should be ideal for heavy fabrics such as blankets. High temperature curing of these fabrics is difficult on account of their thermal insulating properties. Adequate stabilization can probably be obtained readily with existing drying equipment.

## Summary

A simple process for wash stabilization of wool fabrics is described. The fabric is impregnated with a melamine resin acid colloid and dried at 200° F. or below. Process variables including curing temperatures, aging prior to washing, kind and amount of acid used in colloid formation, and resin solids add-on are explored.

A higher resin add-on is needed at low curing temperatures than at high temperatures to achieve equal shrinkage control. The advantages of low curing temperatures are discussed.

## Acknowledgment

The assistance of C. R. Williams, M. A. Goodwin, and K. D. Wiswell in the conduct of this investigation is most gratefully acknowledged.

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# A Survey of Soluble Chemically Modified Cotton Fibers[1]

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**Abstract**

Many cellulose derivatives are known to be water- or alkali-soluble. The solubility of these derivatives which are principally esters and ethers has been found to be a function of the degree of polymerization, the nature of the substituent group, degree of substitution, method of preparation, and type of solvent. A few soluble fibers have been prepared from cotton in which the fibrous form of the cotton is retained during the preparation; that is, the cellulosic hydroxyl group has been chemically modified to a group which confers solubility to the fiber. Hydroxyethylation, carboxymethylation, and oxidation are examples of such procedures and details of the processes are given.

Factors affecting the solubility of chemically modified cotton are discussed. Among these are the mechanism of solution of a modified fiber; and the problems of uniformity of treatment encountered in the chemical modification of cotton fiber, yarns, and fabric.

Some of the present uses of soluble fibers and possible future uses are discussed.

THE chemical modification of cellulose to yield water- or alkali-soluble derivatives is an old and important industrial process. For many years tons of soluble cellulose derivatives have been produced for use as sizes, starch substitutes, fillers, binders, plastics, soap substitutes, food thickeners, and for similar uses. Materials which are produced in rather large volume are methyl-, ethyl-, hydroxethyl and sodium carboxymethyl cellulose. However, chemical modification of the cotton fiber to produce soluble derivatives with retention of the fibrous form of cotton is rather new. Apparently only two soluble cottons have so far reached commercial production, and both are produced in rather small volume. One of these is a soluble cotton gauze, an oxycellulose made by oxidation of the cotton with nitrogen dioxide. The other is a soluble cloth used as a foundation fabric in the manufacture of lace. It is prepared by the oxidation of cyanoethylated cotton with chromic or periodic acid.

The principal soluble noncellulosic fibers in commercial use at the present time are the alginates, produced from seaweed, and silk, both of which are alkali-soluble and water-insoluble, and an extruded polyvinyl alcohol fiber which is water-soluble.

Several methods of preparing soluble cellulose derivatives are available, and some of these methods have been adapted to the preparation of soluble cotton fiber. Although other methods could probably be used, the cost of such preparation is one of the principal factors limiting commercial production and industrial use of such material.

Before discussing the present status of chemically modified soluble cotton fibers, it is appropriate to review the various types of cellulose derivatives which are water- or alkali-soluble and give consideration to their possible use as soluble fiber. Although only a few of them have been prepared in the form of soluble cotton fibers, it is possible that more soluble fibers will be made in this way in the future. Of course, practically all cellulose derivatives are water-soluble if the degree of polymerization (D. P.) is very low. However, in the following section, the discussion is of derivatives in the general range which might conceivably give fibrous products.

## Water- and Alkali-Soluble Cellulose Derivatives

### *Xanthate*

Probably the most important of all soluble cellulose derivatives is cellulose xanthate because it is the important intermediate in the preparation of vis-

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cose rayon [15]. It is prepared by the reaction of alkali cellulose with carbon disulfide to yield the sodium salt of the cellulose ester of dithiocarbonic acid, Cell—O—CS—S—Na. However, there is a ripening action of the xanthate with increasing time which would lead to a weakened fiber. Because of this instability, it is evident that the xanthate offers little promise of being used as a soluble textile fiber.

*Inorganic Esters*

Cellulose nitrate is the most common of the inorganic esters of cellulose, but it is not soluble in water and breaks down in the presence of strong alkalies. Cellulose phosphate, although quite stable toward alkali, is insoluble in water or alkali [25]. Cellulose sulfate, with a degree of substitution (D. S.) approaching 3, has been prepared from chloro-sulfuric acid and cellulose in the presence of pyridine and is soluble in water [10]. The sodium salt has been produced commercially in this country [29]. With a D. S. of only 0.33, the neutral salt is soluble in hot and cold water, insoluble in organic solvents, and stable to alkalies even at elevated temperatures. If degradation of the cotton could be minimized, cellulose sulfate would be the most promising of these esters.

*Organic Esters*

The cellulose esters of monocarboxylic acids have been studied rather completely and in general have been found to be insoluble in water and dilute alkalies. However, Fordyce [9] has patented the preparation of a water-soluble cellulose acetate with 13 to 19% acetyl content, and a study of the preparation and properties of these types of far-hydrolyzed cellulose acetates has been made by Malm and coworkers [21]. Cellulose esters of two of the dicarboxylic acids have been found to be soluble in alkali though not in water, for example, the half-esters of phthalic and succinic acids [22]. Except for such dicarboxylic compounds, the cellulose esters are not promising as water- or alkali-soluble fibers. Of course, esters such as cellulose acetate have been used for soluble fibers where solubility in organic solvents is satisfactory, but such fibers are not within the scope of this paper.

*Cellulose Ethers*

The most promise for soluble fibers is found among the cellulose ethers. A number of soluble cellulose ethers are in commercial use. Many of the lower alkyl ethers, especially those bearing a hydrophilic or functional group, are soluble [1]. As mentioned below, the length of the cellulose chain has a considerable effect upon solubility. The short-chain alkyl ethers, such as the methyl and ethyl ethers, prepared by the alkylation of soda cellulose, may be either or both water- and alkali-soluble. The ethyl ether is more soluble than the methyl, and in addition is soluble in organic solvents at higher degrees of substitution. The higher homologues of the alkyl celluloses have been prepared but, due to the hydrophobic nature of the alkyl substituents, they are soluble in water or dilute alkali.

Examples of soluble cellulose ethers containing functional groups are hydroxyethylated, carboxymethylated, and carboxyethylated celluloses. One method of preparing hydroxyethyl cellulose fibers is by the action of ethylene oxide on cellulose with dilute sodium hydroxide as a catalyst [16]. Carboxymethylated cotton fibers may be prepared by the use of chloracetic acid in the presence of strong sodium hydroxide [7]. Carboxyethyl cellulose can be prepared by the addition of unsaturated compounds such as acrylonitrile [3, 4] or acrylamide [32] in a Michael-type condensation, followed by hydrolysis of the nitrile or amide group to carboxyl.

Cyanoethylcellulose may also be prepared by the reaction of acrylonitrile with cellulose. MacGregor has reported that cyanoethylcellulose prepared from xanthate may be water-soluble, alkali-soluble, or organic solvent-soluble [18, 20]. He found the product to be insoluble in water, but soluble in dilute alkali in the range of substitution of 0.2–0.3 cyanoethyl groups per anhydroglucose unit; soluble in water, dilute alkali, and dilute acid at D. S. 0.7–1.0, but insoluble in alcohol or acetone; and soluble in acetone and other organic solvents in the range of D. S. of 2.5–3.0. In the study of cyanoethylated cotton at the Southern Regional Research Laboratory, water and alkali solubility was not observed in samples with D. S. up to 2.7 [8]. The difference in solubility between cyanoethylated cotton and cyanoethylated rayon lies in the greater degree of polymerization of cotton. Rayon, with its much shorter chain lengths, is more readily solubilized.

Another cellulose ether, sulfoethylated cellulose, has been described by Timell [28]. It is prepared by the reaction of sodium 2-chloroethyl sulfonate with alkali cellulose. The free acid at D. S. of 0.3

is soluble in water, and in contrast to carboxymethylcellulose forms no water-insoluble salts. The sodium salt is alkali-soluble at a D. S. of 0.1, and water-soluble at 0.2.

*Oxidized Cellulose*

A completely soluble cellulose derivative has been prepared by the oxidation of cellulose with nitrogen dioxide[14]. This process has been used commercially to produce a soluble gauze for dressing wounds. The gauze, left in the wound, is gradually dissolved in the blood. A disadvantage of this type of oxycellulose is the large loss of strength with continued degradation on storage.

Alkali-soluble oxycelluloses are also produced by the action of chromic and periodic acid. A commercially available soluble fabric, "Solvotex,"[3] is prepared by the oxidation of partially cyanoethylated cotton [33]. The strength of this fabric is good.

*Acid-Soluble Derivatives*

Acid-soluble derivatives of cellulose are rare. Some, however, have been reported in the literature. Breslow [5] has described the preparation of certain cellulose urethanes which are soluble in dilute acids without degradation. The action of p-dimethylaminophenyl isocyanate on hydroxyethylcellulose resulted in hydroxyethylcellulose p-dimethylaminophenyl carbamate, which was soluble in 0.1 *N* hydrochloric acid and in 5% acetic acid. Ethylcellulose-$\beta$-pyridyl carbamate and cellulose acetate-$\beta$-pyridyl carbamate were prepared by the action of nicotinyl azide on the appropriate cellulose derivatives. These products were both soluble in 0.1 *N* hydrochloric acid but insoluble in 5% acetic acid.

Amphoteric cellulose derivatives, soluble in water, alkali, and acid, have been disclosed in the patent literature by Vaughan [31]. Carboxymethylcellulose, carboxyethylcellulose, and sulfoethylcellulose are reacted with dialkyl aminoalkyl halides, such as diethylaminoethyl bromide hydrobromide or dimethylaminoethyl chloride hydrochloride to yield the desired product.

Because of the degradation resulting from the action of acid on cellulose, it seems probable that the acid-soluble derivatives of cellulose have little more than academic interest in the preparation of soluble cotton fibers.

[3] The mention of trade names and products in this paper does not imply their endorsement by the Department of Agriculture over similar products not mentioned.

In summary, then, it appears that cellulose sulfate, oxidized cellulose, and certain of the cellulose ethers offer the most promise in the development of soluble cotton fibers.

## Factors Determining the Solubility of Cellulose Derivatives

The cellulose molecule itself is, of course, insoluble in both water and dilute alkali. Solubilization may be achieved in certain special solvents such as 72% sulfuric acid, sodium zincate solution, cuprammonium hydroxide, and cupriethylenediamine solution. Most of these reagents, however, form complexes which are soluble, rather than the cellulose alone actually going into solution. For example, Reeves [24] has shown that solubilization of cellulose in cuprammonium hydroxide solution is accomplished by complex formation of the copper with the two hydroxyl groups at the 2 and 3 positions and with these only.

Cellulose derivatives may be either soluble or insoluble depending upon the degree of polymerization, nature of the substituent group, degree of substitution, type of solvent, and method of preparation.

The degree of polymerization of the cellulose derivative is of special importance in determining solubility. The shorter chain lengths of cellulose are more easily solubilized than the cellulose of high D. P. In general, lower substitutions will affect solubility more on the shorter chains than on the higher molecular weight long chains. In the case of soluble fibers, however, there is a practical limit to the amount of loss of D. P. which can occur, with retention of useful textile properties by the fiber.

The chemical nature of the substituent group greatly affects solubility. Cellulose is hydrophilic, whereas benzyl or long-chain aliphatic groups, whether ester or ether, are hydrophobic and tend to dissolve in hydrocarbon solvents. These two effects oppose each other in the cellulose derivative, and therefore the properties of the derivative depend greatly upon the nature of the substituent groups. In cellulose ethers, if the substituent bears strongly polar groups, such as hydroxyl or carboxyl, their effect on the properties of the cellulose derivative is pronounced in the direction of water and alkali solubility.

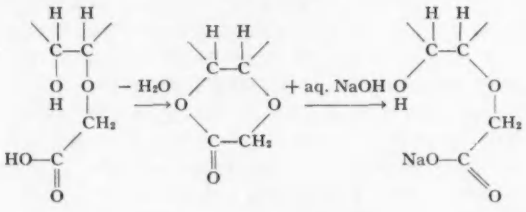
It has been pointed out by Jahn [12] that benzylcellulose, for example, shows solubility at low degrees of substitution in nonpolar solvents. However, the presence of large nonpolar groups, such as

benzyl or butyl, prevents water and alkali solubility, whereas ethylcellulose of low degrees of substitution is readily soluble in water or alkali.

At approximately equal D. P., ethylcellulose becomes water-soluble at a lower degree of substitution, about 1.2, than methylcellulose, which requires a D. S. of approximately 1.8 for good solubility. The larger ethyl groups push the cellulose chains further apart than the methyl groups, causing a greater weakening of the hydrogen bonds between the chains, and permitting water molecules to hydrate and disperse them. The strongly polar groups, such as hydroxyl and sodium carboxyl, have greater hydrating power, and, therefore, effect solubility at lower degrees of substitution.

Cellulose derivatives bearing the carboxyl group, in the free acid form, such as carboxymethylcellulose, carboxyethylcellulose, and oxycellulose, are water-insoluble, but become soluble in dilute alkali which forms the alkali metal salt.

It would seem that the acid form of the cellulose derivative would also be soluble in water since it should hydrate readily. In order to explain these observations, Chowdhury [6] has presented the theory that the acid form of the cellulose derivative forms a lactone ring with unreacted hydroxyl groups of the cellulose molecule on drying, which gives an insoluble product. In alkali, the rings are opened, yielding the sodium salt which is soluble.




In addition to the nature of the substituent, the method by which the substitution is effected is also of importance in the solubility properties of the derivatives. It has been pointed out by Bock [2] that when cellulose is ethylated in a quaternary ammonium base solution, complete water solubility is obtained with a D. S. as low as 0.6–0.7, whereas ethylcellulose prepared from fibrous alkali cellulose does not exhibit water solubility until a D. S. of 1.3–1.5 has been reached. The explanation, which is now almost universally accepted, is that the substituent groups are more uniformly distributed along the cellulose chains when reaction takes place homogeneously in solution, than when the reaction is heterogeneous. A smaller number of solvent groups is necessary if uniformly distributed than when some areas are completely converted but others are still mainly unreacted portions of cellulose.

## Preparation of Soluble Cotton Derivatives

The following section describes the laboratory preparation of some typical soluble cotton derivatives, hydroxyethylated [16], carboxymethylated [7], and oxidized-cyanoethylated cottons [33].

### *Hydroxyethylated Cotton*

Two yards of 80×80 bleached cotton print cloth (4 oz./sq. yd.) was cut to half-width and soaked in a 10% sodium hydroxide solution containing 0.1% Alkamerse R[3] wetting agent. The two pieces of cloth were padded to about 88% pickup of caustic solution and rolled together with alternate layers of glass cloth (to ensure uniform circulation and to prevent localized overheating during treatment), and placed in a reaction tube connected to a solution reservoir and heat exchanger. The cloth was then treated with a circulating solution of about 4% ethylene oxide in carbon tetrachloride at 55° C. for 2 hr.

After the reaction was concluded, the cloth was removed from the reaction tube, soured with dilute acetic acid, washed with water and air-dried. The treated cloth was analyzed and found to have a substitution of 0.61 hydroxyethyl group per anhydroglucose unit. Breaking strength was 94% of the original. The sample was highly swellable in water and soluble in dilute sodium hydroxide.

The ethylene oxide content of the treating solution was checked before and after reaction. An aliquot (5 ml.) of the solution was shaken with 25 ml. of a solution of 0.5 *N* hydrochloric acid saturated with calcium chloride and back titrated with standard sodium hydroxide solution. The ethylene oxide content was 3.7% at the beginning of the reaction and 1.7% at the end. It is believed that if pressure equipment were used, higher concentrations of ethylene oxide would be possible and the result would be higher substitutions and greater solubility.

### *Carboxymethylated Cotton*

One pound of 12/5 grey cotton thread was purified by pressure-boiling with 2% sodium hydroxide

under 15 p.s.i. for 5 hr. After washing and drying, the thread was made into a loose skein and soaked in 20% monochloracetic acid. It was centrifuged to about 65% pickup and then placed on a semi-pilot plant scale frame-type mercerizer [11] and rotated through a 50% solution of sodium hydroxide, allowing some initial shrinkage to obtain good penetration. After about 10 min., the skein was rotated through a 5% solution of acetic acid in alcohol, and then through alcohol alone. When neutralized, the thread relaxed and could be stretched to its original length. After drying the skein, the process was repeated, except that 50% monochloroacetic acid followed by 50% sodium hydroxide was used. The thread was readily soluble in water and dilute alkali. Substitution (D. S.) was 0.74 carboxymethyl groups (sodium) per anhydroglucose unit.

If mineral acids are used for neutralization instead of acetic acid, the carboxymethyl groups will be in the acid form, soluble in dilute alkali and insoluble in water. In this case, the by-product salts may be washed out with water; the product will be stiffer with a slightly harsh hand. In either case, breaking strengths are at least 80% of that of the original thread.

*Oxidized-Cyanoethylated Cotton*

The method of solubilizing cyanoethylated cotton, as described by Weisberg [33], was used. A skein of 12/5 grey cotton thread was cyanoethylated to a nitrogen content of 6.1%, as described by Daul et al. [8]. This modified thread was then treated with 5% chromic acid solution at room temperature for 1 hr., washed with water, and dried. The product was soluble in dilute sodium hydroxide solution, whereas the cyanoethylated sample was insoluble in boiling 10% sodium hydroxide solution. A practical advantage of this process is that the product may be washed easily and inexpensively with water rather than with nonaqueous solvents as is necessary with water-soluble products or when alkali is present.

## Some Factors Affecting the Solubility of Chemically Modified Cottons

*Structure of the Cotton Fiber*

Due to the structure of the cotton fiber and the nature of the cellulose molecule, there are certain restrictions on the solubility of a modified cotton. The fiber must swell, break the restaining winding layer and primary wall, disintegrate, and go into solution. Only about 50% of the primary wall is cellulosic [30]. If complete solubility is required, the noncellulosic constituents must be removed prior to chemical modification of the fiber. This may be accomplished by pressure boiling or by extraction with monoethanolamine. The effect of such purification is shown in the paper of Daul, Reinhardt, and Reid [7] where photomicrographs of carboxymethylated cotton fibers going into solution are shown. Fibers from a sample purified before treatment dissolved almost completely, while those from a sample not purified merely disintegrated, leaving some undissolved remnants.

Cotton, being a high polymer, naturally solubilizes very slowly when chemically modified, unless it is badly degraded. The high D. P. greatly retards the rate of solution and sometimes it is not possible to achieve solubility at all. An example of the latter is the aforementioned case of water and alkali solubility of cyanoethylated rayon reported by MacGregor [18, 20] in contrast to the insolubility of cyanoethylated cotton found at this laboratory [8].

The orientation of the crystalline and amorphous areas of the cotton fibers also bears upon the solubility of its derivatives. The ratio of crystalline to amorphous regions is higher for cotton than for most other forms of cellulose. Thus certain areas of the fiber are not accessible to most reagents unless these regions are opened by some kind of pretreatment. Uniformity of reaction throughout the fiber is thus a little more difficult to attain than with certain other starting materials.

*Non-Uniformity of Treatment*

Retention of the fibrous form of cotton upon the chemical modification of fiber, yarn, or fabric presents peculiar problems for each. These problems increase in magnitude when the modified cotton is soluble in water or dilute alkali.

Fiber is the most difficult to treat in that there is greater tendency for matting, channeling, and poor circulation with consequent localized overheating and gelatinization during treatment and washing. Also the changed fiber characteristics make processing, such as spinning and weaving, very difficult if not impossible. It is very difficult to get a uniform product on treatment of fiber.

Yarn treatment, if it cannot be accomplished in a continuous process, is usually carried out in skein form. Sometimes it is possible to do this on a stand-

ard skein mercerizer. Here again the problem is one of uniformity of reaction. As previously stated, proper purification greatly facilitates reaction. The twist of the yarn interferes with uniformity, especially if the yarn swells during reaction.

Tightness of twist also makes it difficult to wash out by-product salts, which must usually be done with nonaqueous solvents. A unique and efficient way of accomplishing this washing has been described recently by Sönnerskog, in the preparation of hydroxyethylcellulose [27]. Alcohol was circulated by means of a pump through the hydroxyethylcellulose and thence through a filter of Amberlite IR-100[3] (a hydrogen-saturated ion exchanger) which continually removed alkali from the alcohol phase. When the alkali content of the pulp was lower than 1%, an amount of "Nacconol acid"[3] was added to the alcohol, and circulation continued. This acid was prepared by the alkylation of benzene with $C_{12}$—$C_{15}$ alkanes from kerosene, after which it was sulfonated. A strong, water-soluble sulfonic acid was obtained which is very soluble in organic solvents as well as water. The sodium salt of Nacconol acid[3] also is very soluble in alcohol. The extraction proceeded quickly, yielding hydroxyethylcellulose of very low ash content.

In fabric, the problem of getting the reactants into the fiber is difficult. The twist of the individual yarns and tightness of weave of the fabric usually restrict the penetration and make swelling uneven. Thus the amount and uniformity of the reaction with the fiber are reduced. Even if good reaction is obtained, these constructional factors hinder washing and removal of reactants and by-product. Also, the restriction of the swelling of the fiber makes solubilization very difficult. This may be illustrated by observing the solution of a single yarn and one in which several knots have been tied.

In experiments at this laboratory, it has been found that soluble yarn woven together with ordinary cotton may be readily removed from the fabric by soaking in water and then pasing through a padder. This procedure may be repeated several times until the soluble fiber has been completely removed. In this way mechanical force aids in freeing the soluble fiber from the fabric.

Treatment of all forms of cotton is accomplished more readily by a loose packing of the material into the reactors. This allows a free circulation of reactants and dissipation of heat.

## Uses of Soluble Fibers

Potential uses for a soluble cotton are indicated by the present usage of various types of soluble fibers. Some of the applications, both commercial and those which have been demonstrated to be apparently practical in research trials, are described below. These uses involve the temporary utilization of such fibers with subsequent dissolution and washing out of the soluble fibers, yarns, or threads.

With this technique, it has been possible to prepare light-weight woolens by blending soluble fiber with the wool and manufacturing in the usual manner [23]. Upon washing, the soluble fiber is removed, yielding a fabric with many tiny air spaces. The result is increased warmth from a very light, lofty material.

By alternating soluble yarn with regular textile yarns in weaving, and subjecting to an afterwash, open-work fabrics and other novelty effects have been achieved. Similarly, it has been possible to knit socks in a continuous string, each sock connected to the next by a band of soluble yarn [23]. The socks are readily separated by disintegration of the connecting soluble yarn.

Seam pucker, which is due to differential shrinkage of the fabric and sewing thread of garments, can be eliminated if the sewing thread is prepared to contain some soluble fiber [34]. The thread is plied with one end of singles yarn of soluble fiber and the remainder of cotton. The garment is sewed as usual with flat seams. On laundering, however, the soluble fiber disintegrates and enables the cotton yarn in the thread to adjust itself when it tends to shrink due to the removal of the soluble single. If the ply is properly designed, taking into account the shrinkage of the fabric as well as that of the thread, the seam will still be flat without the undesirable puckered appearance.

With soluble fiber, it has been possible to prepare nonwoven fabrics [19] and to fix seams temporarily with simple removal of the basting thread later. A process for printing a wide range of cloths, heretofore difficult to print, has been made possible by temporarily fixing the pile of the cloth with soluble yarn [13]. Lace can be made on ordinary machinery by "embroidering" on soluble cloth and later dissolving out the backing material. Formerly, silk was used for this purpose, dissolution being carried out with strong alkali; now, however, silk has been largely replaced by a soluble "cotton" [33].

A soluble yarn is used in the manufacture of crepe nylon. A tightly wound nylon and soluble cotton thread is used in the cloth at closely spaced intervals. The nylon is set by heat, and the soluble portion dissolved.

A water-soluble filter for trapping airborne microorganisms has been used in England for the study of respiratory irritants [26]. A wad of sterile water-soluble fiber is placed in a special filter tube mounted on the rooftop and a known volume of air pumped through it. The filter-fiber is removed and dissolved in sterile water, which is made to the desired volume after complete solution. Aliquots of this solution are plated out on culture media for incubation and counting.

Another use of soluble fiber has been disclosed in a patent describing a method of producing skinless frankfurters [17]. In one method of manufacture, the frankfurters are produced in water-insoluble sausage casings which are tied together in links using a mercerized cotton thread. It has been necessary to remove these link-ties by hand (the only non-mechanized part of the manufacturing process). However, the patent claims that, by using a water-soluble string, such as carboxymethylated cellulose, the ties can be removed at the end of the cooking operation when the casing is fed into a casing splitting machine. The links are retained in the desired shape during cooking, but at the end, the ties are so weakened or completely disintegrated that they can be readily removed by the machine. A practical difficulty in the use of this process would appear to be the necessity of keeping the soluble string absolutely dry during the period of its use in the linker machine.

With the interest of industry turning more and more to automation, utilization of soluble fibers is indicated as the answer to many problems of process design. The cost of a soluble fiber will in many cases be considerably less than the labor involved in the removal of an insoluble temporary fiber.

## Summary and Conclusions

In conclusion, this survey shows soluble fibers already in use in many phases of the textile and other industries, with new uses indicated as a result of continued research. Chemical modification of cotton has produced a number of fibrous, soluble derivatives. The preparation of soluble hydroxyethylated, carboxymethylated and oxidized cotton has been demonstrated. Others will probably be prepared in the future by adaptation of methods which have already yielded soluble nonfibrous cellulose derivatives.

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# Identification of Sizings on Fabrics Woven from Synthetic Filament Yarn

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## Introduction

The number and types of sizings used on filament synthetic yarns is constantly increasing, thereby requiring the commission dyehouse to be constantly alert to the potential desizing difficulties that may accompany each new sizing. The critical importance of this point may be illustrated by the following examples:

*Stymer S* (Monsanto), a polystyrene resin, extensively used in sizing filament acetate warps, becomes insoluble when acidified and may precipitate out of solution and deposit on the cloth if not thoroughly rinsed after an alkaline scour, before giving any acid treatment. Should greige cloth containing Stymer S be given an initial acid treatment, it then becomes very difficult to remove the Stymer S without risking saponification of the acetate yarn by the strongly alkaline conditions necessary to solubilize it. Several other sizings are similarly precipitated by acid media.

Polyacrylic acid becomes very tenaciously set on nylon if the fabric is heat-set before this sizing has been removed.

Other sizings are not affected by heat-set treatments and may be readily removed even if heat-set before scouring.

Knowledge of the type of sizing present on the greige fabric will, in many cases, determine the method of handling it by the commission dyehouse. Specifications as to the sizing used on greige goods are often provided by the mills who weave the cloth, but oftentimes these specifications are not forwarded to the dyehouse. Some weaving mills do not identify the sizings they have used. Occasions have also arisen where the weaver's specification has proved to be incorrect, apparently due to an error in paper work.

Due to the increasing importance of knowledge of the type of sizing present on each fabric a dyehouse processes, it was found necessary to develop a qualitative procedure to identify the various sizings by a method which was accurate, yet rapid and simple in performance and evaluation.

## Experimental Procedure

This work was limited to sizings encountered on fabrics woven from synthetic filament yarns. The following sizings were tested:

1. GELATIN, most used on acetate and viscose warps, is also found on a few Orlon[2] fabrics. It has recently been found on a Perlon sheer fabric which was woven in Germany.

2. STARCH is not generally found on filament yarns. It has recently been encountered on an all viscose crepe fabric which was woven in Japan.

3. STYMER S (Monsanto), a polystyrene resin, is

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[2] Du Pont acrylic fiber.

widely used on acetate fabrics but has not been seen in use on other fibers.

4. STYMER R (Monsanto) is a vinyl copolymer. It is the sodium salt of Stymer LF, which makes it water-soluble for use as an easily removable sizing. It is a new sizing which has been found only on Dacron [3] at the present time.

5. POLYACRYLIC ACID is marketed under the following trade names:

Orthocryl 25 (American Aniline & Extract Co.)
Good-Rite TS-20 (B. F. Goodrich)
Acrysol A-1 (Rohm & Haas)

It is widely used on nylon fabrics. Often very small amounts are found on very lightweight flat and puckered nylon fabrics.

6. POLYMETHACRYLIC ACID is marketed under the trade name:

Tyze (Du Pont)

This sizing is no longer being sold, but large amounts are apparently still in the hands of weavers. It has been found on nylon fabrics.

7. POLYVINYL ALCOHOL is marketed under the following trade names:

Elvanol (Du Pont)
PM-90 (American Aniline & Extract Co.)

It has been found on nylon and on samples of Perlon which were woven in Germany.

8. STYMER LF (Monsanto) is an alkali-soluble vinyl copolymer. It is being used on so called "loom-finished" acetate fabrics by conversion into ammonium salt in slashing.

9. ELVALAN [4] (Du Pont) is an alkali-soluble vinyl copolymer. It is being used on loom-finished acetate fabrics, for which use it is solubilized in slashing with ammonium hydroxide, leaving a water-insoluble finish when the ammonia is driven off during drying. When used as a sizing on Dacron, it is solubilized in slashing with sodium hydroxide or sodium carbonate, leaving a water-soluble size on the yarn.

10. SPINNING OILS, applied by manufacturers of the yarns and by throwsters, are quite generally encountered, and certain lighter weight nylon fabrics were found to be free of conventional sizings and contained spinning oils only.

11. WEAVING LUBRICANTS, such as Avconit WD (American Viscose Corp.), were also found, either alone or in conjunction with conventional sizings.

[3] Du Pont polyester fiber.
[4] Formerly known as Elchem 1273.

Other trade-name products, chemically identical to those sizings indicated above, may be in use but were not encountered in this necessarily limited study. The trade-name products listed above have all been used in the development of the test procedure.

Simple staining, or other tests which may be run directly on the greige fabric, proved to be inadequate and also were of little value on those fabrics which contained a large amount of throwster tint.

The extraction method of Skinkle [9, 10] was modified to use a regular Griffin low-form 400-ml. beaker since no volatile solvents were used in the extractions. A round-bottom 250-ml. flask, through which cold water is circulated, was placed over the beaker and was used during the short reflux operation.

Fabric spotting tests [2, 8] were used as confirmatory tests where they were found to be reliable.

In general, precipitation and color reaction tests on the distilled-water extract [1, 5, 6, 7] were found to be the most reliable and rapid for routine use. Titrations with N/10 NaOH were found to be valuable for determination of acidic sizings [3, 4]. But they required careful interpretation, especially for lighter weight fabrics which may contain very small amounts of acidic sizings used in conjunction with the essentially neutral spinning oils and weaving lubricants.

The water-insoluble loom-finished sizings were not removed in sufficient quantities by distilled water to permit positive tests, but were removable by refluxing with very dilute alkaline solutions.

The character of the precipitates formed in the reactions is important. The following definitions apply to the precipitates and solutions described in the tests.

A lumpy precipitate is one in which the particles coalesce to form large aggregates, opaque in appearance, which remain as large discrete particles even when shaken vigorously.

A gelatinous precipitate does not show discrete particles, has a translucent appearance, and readily disperses on shaking.

A turbid solution is free of precipitate and is translucent almost to the point of transparency.

A milky solution is free of precipitate and opaque or barely translucent in appearance.

Chart 1 shows the general analytical scheme that was used.

**Chart 1**

Extract 10-g. sample of greige cloth in 200 ml. of distilled water for 10 min. at boil under reflux. Filter through coarse filter paper and run tests on 5 ml. of extract in test tube.

*Test 1.* 1 drop glacial acetic acid, heat, 2 drops 50% NaOH, 3 drops Fehling's soln., warm

- Red-violet color — GELATIN or CASEIN
- Pale blue or greenish blue solution = others — *Test 2.* 1 drop of dilute iodine soln.
  - Blue or purple color — STARCH
  - Orange or reddish color = others — *Test 3.* HCl, $La(NO_3)_3$, $I_2$, $NH_4OH$
    - Light red-brown or deep reddish-brown ppt. — STYMER R or Na salt of ELVALAN
    - White or very pale yellow ppt. = others — *Test 4.* 1 ml. conc. $H_2SO_4$
      - Gelatinous or lumpy ppt. — STYMER S or POLYMETHACRYLIC ACID — *Test 5.* Titrate extract with $N/10$ NaOH
        - More than 1.0 ml. NaOH consumed — POLYMETHACRYLIC ACID
        - Less than 1.0 ml. NaOH consumed — STYMER S
      - Clear, turbid, or milky, no ppt. = others — *Test 6.* 5 ml. $Ba(OH)_2$ soln.
        - Lumpy or gelatinous ppt. — POLYACRYLIC ACID
        - Clear or turbid, no ppt. = others — *Test 7.* 5 drops Tannin soln.
          - Lumpy ppt. — POLYVINYL ALCOHOL
          - Clear or turbid, no ppt. = others — Reflux fresh cloth sample in 200 ml. of distilled $H_2O$ to which 1 ml. of 25% NaOH soln. has been added. *Test 8.* HCl, $La(NO_3)_3$, $I_2$, $NH_4OH$
            - Red-violet to deep reddish-brown ppt. — STYMER LF or ELVALAN 1273 — *Test 9.* 1 ml. conc. $H_2SO_4$
              - Granular ppt. — STYMER LF
              - Milky soln. no ppt. — ELVALAN 1273
            - White to pale yellow ppt. — SPINNING OILS or WEAVING LUBRICANTS

The eleven sizings listed above can be identified by the following methods.

Extract a 10-g. sample of greige cloth in 200 ml. of *distilled water* for 10 min. at boil under reflux in a 400-ml. low-form Griffin beaker, using a round-bottom 250-ml. flask to cover the beaker. Cold water is circulated through the flask as a means of cooling. With heavy-weight acetate fabrics, porcelain chips may be necessary to prevent bumping, but other fibers do not seem to be as prone to bumping. Filter through rapid filter paper. Perform the following tests in the order specified.

*Test No. 1*

Place 5 ml. of extract in a test tube, add 1 drop of glacial acetic acid, and heat carefully. Add 2 drops of 50% NaOH solution, then add 3 drops of Fehling's solution and warm.

*Note:* If tint from greige goods is present in extract, it must be destroyed before running Fehling's solution test (Test No. 1). Add *very minute* amount of sodium hydrosulfite to 5 ml. of hot extract solution until all tint is destroyed, then run Test No. 1 in regular manner. *Do not use excess hydrosulfite.*

GELATIN: red-violet color. Run confirmatory tests.

OTHERS: pale blue or greenish blue. See Test No. 2.

*Confirmatory tests for gelatin*

A. Place drops of Monsanto Solution A on dry sample of greige cloth, followed by two drops of methanol.

GELATIN: blue halo with purple or blue center.

OTHERS: red-violet halo with blue center.

B. Add 5 ml. of saturated zirconium sulfate solution to 5 ml. of extract and shake.

GELATIN: heavy, lumpy precipitate.

OTHERS: clear, turbid, or gelatinous precipitate (not lumpy).

C. Add 5 drops of tannin solution to 5 ml. of extract and shake.

GELATIN, STYMER R, POLYVINYL ALCOHOL; white or brown precipitate.

OTHERS: clear or milky, no precipitate.

D. Add 10 drops of a saturated copper sulfate solution to 5 ml. of extract and shake.

GELATIN: milky solution, no precipitate.

OTHERS: clear or precipitate, not milky.

E. Dip sample of cloth in $CuSO_4$ solution for a few seconds, then remove and immerse in 1% NaOH solution for a few seconds. Remove and allow to stand a few minutes on a spot plate.

GELATIN: violet color on cloth.

OTHERS: blue-green color on cloth.

*Test No. 2*

Cool 5 ml. of extract and add 1 drop of dilute iodine solution and shake.

*Note:* If greige tint is present, destroy as described in Test No. 1.

STARCH: blue to purple color. Run confirmatory tests.

OTHERS: pale orange or yellow. Possible red color if more than 1 drop of iodine solution used. See Test No. 3.

*Confirmatory tests for starch*

A. Apply a few drops of dilute iodine solution to cloth.
   STARCH: blue color.
   OTHERS: orange to reddish color.

B. Evaporate 10 ml. of extract to dryness and add 1 drop of dilute iodine solution.
   STARCH: blue to purple color.
   DEXTRINE: brown color.

*Test No. 3*

Cool 5 ml. of extract and add in the following order: 2 drops of conc. HCl, 5 drops of 5% Lanthanum Nitrate solution, 20 drops of dilute iodine solution, 10 drops of conc. $NH_4OH$ and shake well.

STYMER R and SODIUM SALT OF ELVALAN: light red-brown to deep reddish-brown precipitate forms rapidly, tends to decolorize on long standing, generally gelatinous precipitate but may be lumpy. No test has been found to differentiate between Stymer R and the sodium salt of Elvalan. A clue as to which of the two is present may be obtained by titrating a 50-ml. sample of the extract as described in Test 5. If a red color develops when the phenolphthalein is added, and before the NaOH titration is started, it is probably the sodium salt of Elvalan, to which an excess of alkali has been added when being solubilized by the slasher. Stymer R is sold as the sodium salt, and its pH is generally such as to require at least 0.1 ml. of $N/10$ NaOH solution. Run confirmatory tests.

OTHERS: white or very pale yellow precipitate. See Test No. 4.

*Confirmatory tests for Stymer R and Na salt of Elvalan*

A. Cool 5 ml. of extract and add 3 drops of dilute iodine solution.
   STYMER R and ELVALAN: deep wine-red color, no precipitate.
   OTHERS: light orange to pale yellow color.

B. Add 5 drops of tannin solution to 5 ml. of extract.
   STYMER R and ELVALAN: heavy gelatinous precipitate.
   OTHERS: clear or lumpy precipitate, not gelatinous.

C. Add 5 ml. of 10% Zinc Sulfate solution to 5 ml. of extract.
   STYMER R and ELVALAN: lumpy precipitate. (Some samples do not precipitate, but become very milky.)
   OTHERS: gelatinous or clear precipitate, not lumpy or milky.

D. Add 1 drop of 5% Lanthanum Nitrate solution to 5 ml. of extract.
   STYMER R and ELVALAN: lumpy precipitate; all samples encountered have given positive results with this test.
   OTHERS: clear, milky, or gelatinous precipitate, possible lumpy precipitate.

E. Add 10 drops of saturated $CuSO_4$ solution to 5 ml. of extract and shake.
   STYMER R and ELVALAN: heavy, lumpy white precipitate. (Some samples do not precipitate in this test but form very milky solutions.)
   OTHERS: blue or white gelatinous precipitate forms slowly, or clear.

F. Evaporate 25 ml. of extract to dryness (don't bake). Place under ultraviolet light.
   STYMER R and ELVALAN: no fluorescence.
   OTHERS: yellow fluorescence.

G. Add 5 ml. of dioxane to residue and heat.
   STYMER R and ELVALAN: soluble.
   OTHERS: insoluble.

H. Add 5 ml. of acetone to residue and heat.
   STYMER R and ELVALAN: soluble.
   OTHERS: insoluble.

*Note:* Test No. 3 is not sensitive to very small amounts of Stymer R or Elvalan but has yielded positive results with fabrics known to be slashed with 1% and stronger solutions of these sizings.

*Test No. 4*

Add 1 ml. of conc. $H_2SO_4$ to 5 ml. of extract, cool, and shake.

STYMER S and POLYMETHACRYLIC ACID: gelatinous or lumpy precipitate. See Test No. 5.

OTHERS: clear, turbid, or milky, but no precipitate. See Test No. 6.

*Test No. 5*

Titrate 50 ml. of extract to phenolphthalein end point (5 drops of indicator) with $N/10$ NaOH solution using a 1.0-ml. graduate pipette (marked to 0.05-ml. divisions at least). While appearing crude, this can be done accurately and much more rapidly than a burette would permit.

POLYMETHACRYLIC ACID will consume more than 1.0 ml. of $N/10$ NaOH solution. Records indicate it will generally consume well over 2.0 ml. Run confirmatory tests.

STYMER S will consume less than 1.0 ml. of $N/10$ NaOH solution. Generally consumes less than 0.5 ml. Run confirmatory tests.

*Confirmatory tests for Stymer S and polymethacrylic acid*

A. Add 5 ml. of saturated $Ba(OH)_2$ solution to 5 ml. of extract.
   STYMER S: gelatinous precipitate forms rapidly.
   POLYMETHACRYLIC ACID: very milky solution, forms lumpy precipitate only after violent shaking.

B. Add 1 ml. of conc. HCl to precipitate (A) above.
   STYMER S: gelatinous precipitate not affected, remains as is.
   POLYMETHACRYLIC ACID: lumpy precipitate becomes more pronounced.

C. Add 5 ml. of 10% $CaCl_2$ solution to 5 ml. of extract.
   STYMER S: heavy gelatinous precipitate.
   POLYMETHACRYLIC ACID: clear, turbid, or possibly lumpy precipitate, no gelatinous precipitate.

D. Add 1 drop of 5% lanthanum nitrate solution to 5 ml. of extract.
   STYMER S: fine gelatinous precipitate.
   POLYMETHACRYLIC ACID: clear or very heavy coarse gelatinous precipitate.

E. Add 5 ml. of saturated zirconium sulfate solution to 5 ml. of extract. Shake and allow to stand 2 min.
   STYMER S: very milky solution, no precipitate.
   POLYMETHACRYLIC ACID: fine gelatinous precipitate, not milky.

F. Add 5 ml. of 10% zinc sulfate solution to 5 ml. of extract. Shake and allow to stand 2 min.
   STYMER S: coarse, white gelatinous precipitate.
   POLYMETHACRYLIC ACID: clear or fine gelatinous precipitate.

G. Add 5 drops of basic lead acetate solution to 5 ml. of extract. Shake and allow to stand 2 min.
   STYMER S: coarse gelatinous precipitate.
   POLYMETHACRYLIC ACID: fine gelatinous precipitate.

*Test No. 6*

Add 5 ml. of saturated $Ba(OH)_2$ solution to 5 ml. of extract and shake.

POLYACRYLIC ACID: lumpy precipitate (sometimes gelatinous if small amount of sizing present) forms rapidly. Run confirmatory tests.

OTHERS: clear or slightly turbid, no precipitate. See Test No. 7.

*Confirmatory tests for polyacrylic acid*

A. Add 1 ml. conc. HCl to precipitate found in Test No. 6 and shake.
   POLYACRYLIC ACID: precipitate dissolves to form clear solution.
   OTHERS: clear or slightly turbid.

B. Add 5 ml. of saturated $BaCl_2$ solution to 5 ml. of extract and shake.
   POLYACRYLIC ACID: lumpy precipitate, sometimes gelatinous, forms rapidly. Addition of 1 ml. conc. HCl dissolves the precipitate and clarifies the solution.
   OTHERS: clear at each stage.

C. Titrate 50 ml. of extract to phenolphthalein end point (5 drops of indicator) with $N/10$ NaOH solution, using a 1 ml. pipette.
   POLYACRYLIC ACID: will consume more than 0.6 ml. of $N/10$ NaOH solution. Records indicate that very lightweight sheers and puckers will consume from 0.6 to 1.0 ml. of NaOH solution, while heavier weight fabrics may consume from 1.5 to 8.4 ml.
   OTHERS: will consume less than 0.6 ml. of $N/10$ NaOH solution. Records indicate the following consumption ranges:
      Polyvinyl alcohol—0.05 to 0.3 ml.
      Gelatin—0.1 to 0.8 ml. (0.4 average)
      Stymer S—0.2 to 0.5 ml.
      Spinning oils—0.05 to 0.1 ml.
      Stymer R—0.05 to 0.2 ml.
      Na salt of Elvalan—0.00 to 0.05 ml.
      Starch—0.05 to 0.1 ml.

Elvalan—0.05 to 0.3 ml.
Stymer LF—0.2 to 0.3 ml.
Polymethacrylic acid—2.9 to 4.6 ml.
Polyacrylic acid—0.55 to 8.4 ml.

D. Add 1 drop of 5% lanthanum nitrate solution to 5 ml. of extract and shake.
POLYACRYLIC ACID: lumpy or gelatinous precipitate.
OTHERS: clear.

*Test No. 7*

Add 5 drops of tannin solution to 5 ml. of extract and shake violently.

POLYVINYL ALCOHOL: very milky and rapidly forms a lumpy precipitate. Precipitate may be white, tan, or brown. Run confirmatory tests.
OTHERS: clear or turbid, no precipitate. See Note below.

*Confirmatory tests for polyvinyl alcohol*

A. Spot fabric with 1 drop of chromic acid solution, then spot immediately in same place with 3 drops of 50% NaOH solution and rub with stirring rod to neutralize all the chromic acid.
With lighter weight fabrics, use two to four layers of cloth when running this test, making certain that the chromic acid and NaOH solutions penetrate all the layers.
POLYVINYL ALCOHOL: full brown colored spot.
OTHERS: orange or yellow spots.

*Note:* If there are no positive tests up to this point, extract a fresh 10-g. sample with 200 ml. of distilled water to which 1 ml. of 25% NaOH solution has been added. Reflux at boil for 15 min. and filter through rapid filter paper.

*Test No. 8*

To 5 ml. of the NaOH extract, add in the following order: 2 drops of conc. HCl, heat to boil carefully in test tube and maintain at boil for 1 min., then add 5 drops of 5% lanthanum nitrate solution, 20 drops of dilute iodine solution, and cool very thoroughly. Then add 10 drops of conc. $NH_4OH$ and shake well.

STYMER LF and ELVALAN: red-violet to deep reddish-brown precipitate. Tends to decolorize on long standing. See Test No. 9.
SPINNING OILS and WEAVING LUBRICANTS (free of protective sizing): white to pale yellow precipitate.

*Test No. 9*

Add 1 ml. of conc. $H_2SO_4$ to 5 ml. of NaOH extract and shake.

STYMER LF: granular precipitate. Run confirmatory tests.
ELVALAN: milky solution, no precipitate. Run confirmatory tests.

*Confirmatory tests for Stymer LF and Elvalan*

A. Add 1 ml. of conc. HCl to 5 ml. of NaOH extract and shake.
STYMER LF: granular precipitate.
ELVALAN: milky, no precipitate.

B. Add 1 drop of conc. $H_2SO_4$, shake and add 10 drops of saturated $CuSO_4$ solution to the 5 ml. of NaOH extract. Shake and allow to stand 2 min.
STYMER LF: fine granular precipitate.
ELVALAN: milky, no precipitate.

*Note:* Spinning oils and weaving lubricants do not give precipitates or positive reactions in any of the tests, but their presence is apparent by the turbidity of the extract solutions when no protective sizing has been found to be present.

It must be borne in mind, while using this test method, that chemically identical sizings will give slightly different reactions when applied by different weaving mills. These differences are largely due to two highly variable factors.

1. The amount of sizing deposited on the yarn.
2. The amount and type of plasticizing agent used in conjunction with the protective sizing.

In the presence of lower amounts of sizing, less precipitate is to be expected, and it is possible that its character may change, i.e., a lumpy precipitate which formed when a large amount of sizing was present may be altered to a gelatinous precipitate in the presence of a smaller amount of sizing. Plasticizing agents, such as oils, wetting agents, softeners, etc., may tend to act as emulsifying agents and thereby retard or prevent the formation of an expected precipitate.

The $N/10$ titration described in Test No. 5 may be profitably performed on all sizings and interpreted in the light of the data supplied in Test No. 6C by bearing the following facts in mind. The highly acidic sizings, polyacrylic and polymethacrylic acids, can be determined quantitatively by this titration. Values in the higher ranges would indicate the presence of a large amount of sizing, and commensurately

heavy precipitates should be expected. The converse would be true if a low titration value was obtained on a sizing which had previously been identified as polyacrylic or polymethacrylic acid. The loom-finish sizings would follow the same trend as the acidic sizings. A higher titration value would indicate the presence of larger amounts of sizing. The Stymer R and Elvalan sodium salt tend to give relatively low titration values, as would be expected with the presence of sodium in each of these sizings. The implications of titration values found with Stymer R and Elvalan sodium salt are discussed in Test No. 3.

*Preparation of Special Reagents*

1. FEHLING'S SOLUTION: 1 to 1 mixture of Solutions A and B is mixed just prior to using. Experience indicates that the combined solution may be prepared in the morning and used for the balance of the day.

*Solution A:* Dissolve 34.6 g. of $CuSO_4 \cdot 5H_2O$ in water and dilute to 500 ml.

*Solution B:* Dissolve 173 g. of Rochelle Salts, $KNaC_4H_4O_6 \cdot 4H_2O$ and 50 g. of NaOH in water and dilute to 500 ml.

2. TANNIN SOLUTION: dissolve 10 g. of NaCl in 100 ml. of water, heat to 150° F., saturate with tannic acid, cool to room temperature, and filter.

3. MONSANTO SOLUTION A: dissolve 1 g. of Neolan Pink BA (Ciba) in 100 ml. of pure methanol. Dissolve 1 g. of Methylene Blue (Ciba) in 50 ml. of distilled water. To 50 ml. of the Neolan solution, add, in order, 44 ml. of pure methanol, 6 ml. of methylene blue solution, and 0.5 ml. of glacial acetic acid. Stir the mixture well and keep in a closed container overnight. Transfer to a dropping bottle, leaving behind any salts or solid dyestuff.

4. DILUTE IODINE SOLUTION: 1 g. iodine and 20 g. of KI in 500 ml. of water.

5. BASIC LEAD ACETATE SOLUTION: 30 g. of lead acetate, 10 g. of Litharge, and 5 ml. of water are stirred together on a water bath until white. Then, 100 ml. of water are stirred in. Allow reagent to settle, then filter.

6. CHROMIC ACID SOLUTION: add 11.8 g. of potassium dichromate and 25 ml. of conc. $H_2SO_4$ to 50 ml. of water. Stir until dissolved.

For convenience in routine work, add 5 ml. of water to test tube, mark with glass-marking pencil, add 5 ml. more water and mark at the 10-ml. level. Several test tubes marked in this manner provide sufficient accuracy and save considerable time in repetitive tests. Experience with this test procedure has shown that a positive answer is usually obtained within 10 min. after completion of the extraction and often in less time.

## Conclusion

A rapid qualitative test method for the identification of sizings currently being used on fabrics woven from synthetic filament yarn has been developed and proven of value in routine laboratory testing over a period of several months. Mixtures of sizings have not been knowingly encountered, and no tests have been developed to determine components of mixtures.

## Acknowledgments

Gratitude is expressed to Hugh E. Zona and Martin F. Crown for their use and criticisms of this test, and to Morton Schlessinger for his encouragement. Thanks are also due the many weaving mills who have supplied fabrics with known sizings.

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# A Comparison of Egyptian and American Methods for Evaluating Cotton Quality[1]

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WITH the increasing use of fiber tests in international trading, questions arise as to the relations between different methods for measuring fiber properties of cotton and the level of testing found in laboratories of different countries. This is particularly true for the measurements of length, strength, and fineness since they are generally recognized as the most important contributors to spinning quality.

The purpose of this paper is to present data obtained on different cottons by the techniques employed at the Giza Spinning Test Mill, Giza, Egypt, and the Southern Regional Research Laboratory, New Orleans, Louisiana, with particular attention to the newer instrumental methods. The results are of primary interest as an aid in correlating test data obtained by different methods and laboratories. The techniques were applied to 12 samples representing experimental and commercial varieties of Egyptian cottons. The results are used also to illustrate how the Giza Spinning Test Mill applies fiber and yarn data in evaluating different cottons and in selecting new varieties for commercial production.

## Cottons

Twelve samples of Egyptian cottons were selected from the 1952 and 1953 crops. Six were commercial varieties—Giza 45, Karnak, Menoufi, Giza 30, Zagora, and Ashmouni, named in order of descending upper quartile length. The new varieties which are being considered as possible replacements for present commercial varieties were Giza 59, Giza 51, Giza 58, Giza 47, Giza 39×30, and Giza 60. All the samples were from the miniature chequers of the breeding branch of the Egyptian Ministry of Agriculture.

[1] A study conducted under the Foreign Operations Administration Point IV program sponsored by the Governments of Egypt and the United States.

[2] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

## Test Methods

Both laboratories maintain the same standard atmospheric conditions for testing, namely 65% relative humidity at 70° F. Therefore test data obtained in both, using the same instruments and techniques on the same cottons, should be comparable.

The instruments used for testing fiber properties in the two laboratories are listed in Table I. It is noted that both use the Micronaire [3] and the Pressley Tester.

At Giza, the Balls Sorter [2] is generally used for measuring length, whereas this instrument is seldom used in the United States. Results obtained with it are therefore of special interest for comparison with Fibrograph and Suter-Webb array data.

At the Southern Regional Research Laboratory, the methods of the American Society for Testing Materials [1] were followed insofar as possible.

**TABLE I. Instruments and Methods Employed at the Giza Spinning Test Mill and the Southern Regional Research Laboratory for Determining Fiber Properties**

| Property | Instruments and methods | |
|---|---|---|
| | GSTM | SRRL |
| Fiber length | Balls Sorter | Suter-Webb Sorter [1, a]<br>Fibrograph [1, d] |
| Fiber strength | Pressley Tester | Pressley Tester [1, c]<br>Stelometer [4] |
| Fiber fineness | Micronaire | Micronaire [1, e]<br>Arealometer [1, f]<br>Suter-Webb Sorter [1, b] |
| Fiber maturity | NaOH swelling (Baer's Sorter) | NaOH swelling (Suter-Webb Sorter) [1, b]<br>Arealometer "D" [1, f]<br>Differential-dye test [1, g] |

[3] Mention of trade names does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over similar products not mentioned.

The manufacturer's instructions were used with the Stelometer [4], which had become available for determining the breaking load and elongation of flat bundles of fibers at a constant rate of loading and at different gauge lengths. For these tests, a gauge length of 2.5 mm. was used.

The fiber and yarn properties of the Egyptian cottons had been determined at Giza before bringing them to the United States. Their fiber properties were again tested by the senior author at the Southern Regional Research Laboratory, but unfortunately the size of the samples did not permit repeating the yarn tests. In the standard spinning tests at Giza all cottons are spun to 60's count with a twist multiplier of 3.60, and the skein strength is determined with a Goodbrand Lea Tester.

## Comparison of Results

### *Length*

The Half Fall (1/2F), obtained from the Balls Sorter diagram, and the Upper Half Mean (UHM), determined by the Fibrograph, are compared with the Upper Quartile Length (UQL), calculated from the Suter-Webb data, in Figure 1. The highest values were obtained with the Balls Sorter and the lowest with the Fibrograph. In general, the Fibrograph and Suter-Webb values were closer together than those of the Suter-Webb and Balls Sorter.

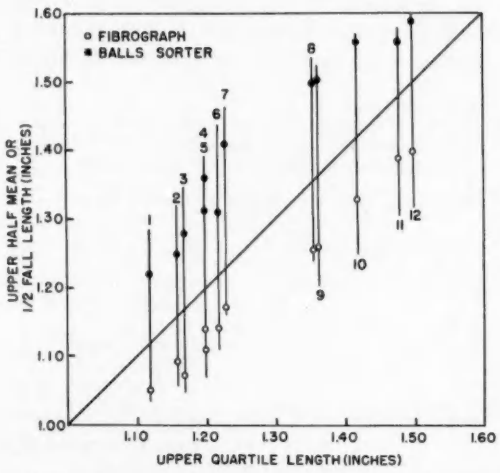


**Fig. 1.** Relation of the Upper Half Mean (Fibrograph) and 1/2 Fall (Ball Sorter) lengths to the Upper Quartile Length (Suter-Webb).

*Egyptian Cottons*

1. Ashmouni
2. Giza 60
3. Zagora
4. Giza 39 × 30
5. Giza 47
6. Giza 30
7. Giza 58
8. Giza 51
9. Menoufi
10. Giza 59
11. Karnak
12. Giza 45

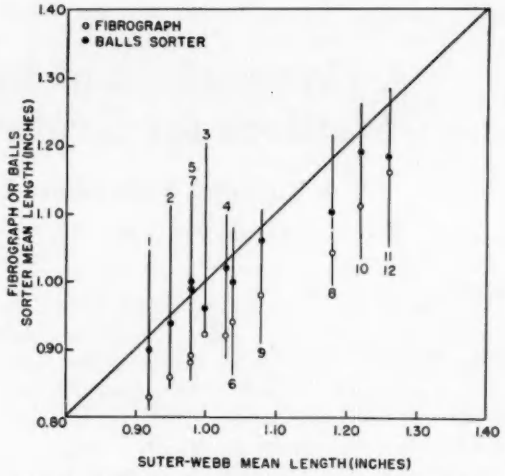


**Fig. 2.** Relation of the mean (Fibrograph) and mean (Balls Sorter) lengths to the mean length (Suter-Webb), Egyptian cottons.

The regression lines for the Half Fall and Upper Half Mean are nearly parallel to that of the Upper Quartile Length but separated by approximately constant terms of + 0.12 and − 0.08 in., respectively. Thus, each method rates the cottons in approximately the same order and with a relatively constant difference.

The mean lengths determined by the three instruments are plotted in a similar manner in Figure 2. The trends are again nearly identical but in different order. The Suter-Webb values are generally the highest with those of the Balls Sorter only slightly lower on the average, and those of the Fibrograph appreciably lower with a deviation of approximately − 0.10 in. from those of the Suter-Webb. The Balls Sorter mean length appears to agree better with the Suter-Webb sorter for short staple and with the Fibrograph for the longer staple cottons.

According to these results, the three instruments rank cottons in essentially the same order as regards length but the values are at different levels. Therefore, any one of these instruments may be used with a high degree of accuracy for comparing different cottons. The possibility of being able to translate values obtained with one instrument to approximate values on another appears promising.

*Fineness*

In Figure 3 the values for hair weight in micrograms per inch, as calculated from the Suter-Webb array data, are plotted against the corresponding values determined with the Micronaires at the Giza and New Orleans laboratories and also against the Arealometer values. The Micronaire values were read from the scale developed for American-Upland cottons, while the Arealometer values, expressed in micrograms per inch, are derived from measurements of the specific area [1, f].

The trends for the different instruments are similar although there is appreciable dispersion. The values obtained with the Arealometer agree more closely with those of the Suter-Webb sorter than do the Micronaire values. This is probably because the Arealometer takes into account the "maturity" factor. The Micronaire values obtained on the Egyptian cottons in the two laboratories show excellent agreement.

Since the Micronaire scales were originally designed for American-Upland cottons, the values obtained with the Egyptian cottons are numerically higher than the Suter-Webb values. However, when the correction factor of 0.8 unit recommended for American-Egyptian cottons [5] is applied, 5 of the 12 samples, including Menoufi and Ashmouni, still differed significantly from the Suter-Webb values. These observations provide further argument for reporting present Micronaire scale readings as an index rather than in weight units.

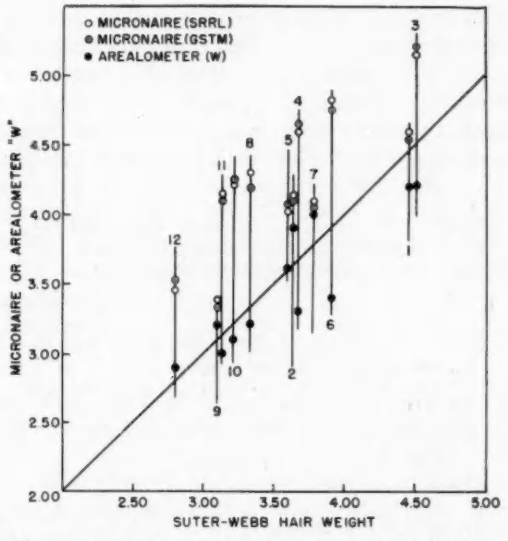


**Fig. 3.** Fineness relationships: Arealometer "W" and Micronaire units versus hair weight per unit length (Array method), Egyptian cottons.

*Strength*

The Pressley Indexes measured at Giza were higher than those obtained in the Southern Regional Research Laboratory, indicating that the two instruments were being operated at different levels. The ranking of the cottons, however, was in the same general order.

In some exploratory tests with the newly developed Stelometer [4], a somewhat different ranking of the cottons was observed when they were tested with a jaw spacing of 2.5 mm., although the general trend was the same as for the Pressley Indexes.

*Maturity*

The cottons were ranked in essentially the same order by results obtained by the sodium hydroxide swelling method [1, b], the Arealometer "D" [1, f], and the differential-dye method [1, g]. As most of the cottons were highly mature, ranging from approximately 80 to 95% by the swelling method, many of the observed differences were within experimental errors. Only a few maturity counts were made by the sodium hydroxide method at Giza. They were all somewhat lower than those made on the same cottons at the Southern Regional Research Laboratory.

## Use of Test Data

The Giza Spinning Test Mill considers Hancock's formula for strength anomaly [3] one of its most useful criteria for discriminating among different cottons and selecting new varieties. This formula which may be expressed as

$$\text{Count-strength product} = K_1 \frac{\text{Staple length}}{\text{Hair weight}} + K_2$$

provides a means for detecting strength differences which may exist after allowing for the contributions of length and fineness. This relationship and its application are discussed by Youssef and Hafez in a recent survey of Egyptian cottons [7]. It is reviewed briefly here since it appears to furnish a simple practical approach that would be helpful in similar investigations. It is applied to the data to illustrate how the Giza Spinning Test Mill uses the relation-

ship in evaluating new varieties of cotton with reference to commercial varieties. In this illustration, however, it must be remembered that only one sample of each variety of cotton was tested. Hence, the results cannot be considered fully representative.

The relationship is based on the observation that the characteristics of Egyptian cottons are such that they generally tend to fall into distinct groups when plotted on scales set up for the various properties. Separations into grouped ranges of values, referred to as "Categories," are more pronounced for certain properties than others, but they are best demonstrated by the staple-length/hair-weight ratio. According to Youssef and Hafez, "These categories create particular ranges of fineness, length, and quality for any spinner to have his choice, while they all retain an adaptive characteristic of the Egyptian environment and particularly in possessing the two valuable attributes of high hair-strength and high hair-maturity which are common to all Egyptian varieties."

When the Egyptian cottons are plotted on this ratio scale, they tend to fall into five distinct categories which are somewhat unevenly spaced but which have few or no values between them. The top of the scale, designated Category I, corresponds to the long-staple fine Sea Island types and the lower end, Category V, includes the Uppers, which are comparable to American-Upland cottons. Commercially, the most important present occupants of the five categories in descending order of length/fineness ratio are Giza 45, Karnak, (vacancy), Giza 30, and Ashmouni. It is anticipated that the vacancy will be occupied by Giza 51.

Youssef and Hafez report the staple-length/hair-weight ratio to be positively correlated with yarn strength by a coefficient as high as 0.93. Some cottons, however, show significant shifts from this relationship; that is, their yarn strength is appreciably greater or less than expected from their length/fineness ratio. Such cottons are considered anomalously strong or anomalously weak. The anomalously strong cottons are obviously the ones of greatest promise in selecting and developing new varieties.

The use of length and fineness as the principal factors in determining the yarn strength to be expected in fine yarns is supported by the findings of Webb and Richardson in their extensive analyses of the relationship between fiber and yarn properties. In their study of 22's and 50's yarns processed from 828 cottons on long-draft roving and spinning equipment [6], they found that the four primary contributors to the 50's yarn strength ranked fiber fineness first, followed by length, strength, and length uniformity. For the 22's yarns, however, the order of fineness and strength was reversed. Since fiber strength is usually an important factor contributing to yarn strength, it is probably one of the most important contributors to the anomalies in the yarn strength detected by Hancock's formula.

Because of the growing tendency to use instrumental methods for evaluating cotton fiber properties, simple correlations were first performed to determine the correlation coefficients for yarn strength versus the different measures of length/fineness ratio. These correlation coefficients are given in Table II. The Suter-Webb data gave slightly higher coefficients than the data of either the Fibrograph or the Balls Sorter. The differences are not great, when the limitations of the present tests are taken into account. In practice, use of either the Fibrograph or the Balls Sorter may be satisfactory, especially considering the greater speed with which the tests are conducted.

Although any one of the six ratios might have been used here, the

$$\frac{\text{Upper Quartile Length}}{\text{Hair Weight}}$$

ratio was selected for demonstration and speculation because of its relatively high coefficient and association with staple length. The lea product [yarn number (60's) × skein strength (lb.)] is plotted against the ratio values in Figure 4. If a somewhat arbitrary limit of ±220 lea-product units (approxi-

**TABLE II. Simple Correlation Coefficients for Yarn Strength (Count-Strength Product) versus Length/Fineness Ratio**

| Length/fineness ratio | Correlation coefficient |
|---|---|
| Upper quartile length/hair weight (Suter-Webb) | 0.93 |
| Upper half mean/Micronaire (Fibrograph-SRRL Micronaire) | 0.79 |
| ½ Fall/Micronaire (Balls Sorter-Giza Micronaire) | 0.77 |
| Mean length/hair weight (Suter-Webb) | 0.96 |
| Mean length/Micronaire (Fibrograph-SRRL Micronaire) | 0.86 |
| Mean length/Micronaire (Balls Sorter-Giza Micronaire) | 0.80 |

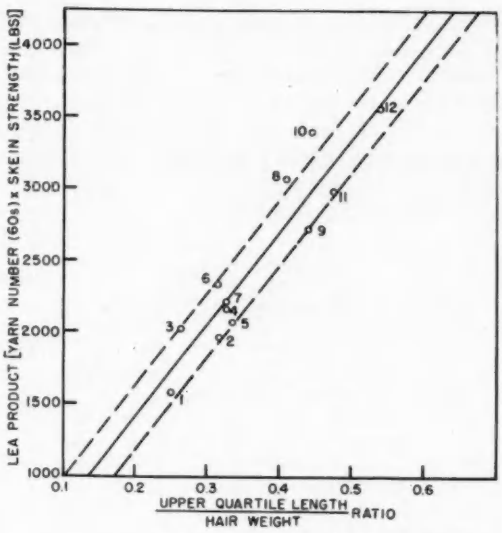


**Fig. 4.** Relation between the ratio $\frac{\text{Upper Quartile Length}}{\text{Hair Weight}}$ and yarn strength (lea product), Egyptian cottons.

mately one standard error of estimate; in the present data approximately 10% of the average lea product—the value which Youssef and Hafez consider the threshold improvement for commercial possibilities of a new variety) is established about the regression line, and cottons within this limit are called "normal," those cottons yielding lea products above these limits may be called "anomalously strong," and *vice versa*. In a close comparison, the cottons can be arranged in descending order according to their deviations from the normal. Suffice here to note that only two cottons—Giza 59 and Giza 51—appear to be in the anomalously strong class while three cottons appear to be on the borderline of the anomalously weak class—Giza 60, Giza 47, and Menoufi.

To compare commercial and experimental Egyptian cottons, a scale of

$$\frac{\text{Upper Quartile Length}}{\text{Hair Weight}}$$

ratios ranging from 0.25 to 0.55 is shown in Figure 5 with the present varieties arranged on the left-hand side of the scale and the experimental varieties on the right. The most important variety in each category, mentioned above, is underscored. The scale shows Giza 45 occupying the top Category No. I. Category II shows the new variety Giza 59 falling below Karnak and opposite Menoufi. Category III, formerly occupied by the almost extinct Giza 7, might be considered to be occupied by Giza 51, although this variety could be included in Category II. Category IV is made up of the medium-staple Egyptian cottons, including Giza 30 and four experimental varieties. In Category V, the Ashmouni category, are Zagora and Ashmouni.

In Figure 6 the cottons in each category are ranked with respect to yarn strength so that the anomalously strong or weak cottons can be detected readily. This diagram is similar in content to Figure 4, except that the broader classifications permit quicker and more general conclusions to be drawn. Although the cottons are arbitrarily separated into categories, those in different as well as those in the same categories may be compared.

A comparison of Figures 5 and 6 leads to the following observations: The general relationship be-

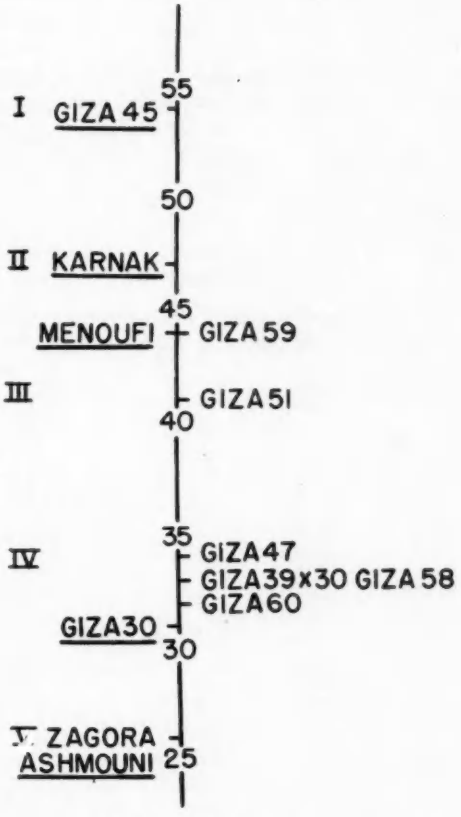


**Fig. 5.** $\frac{\text{Upper Quartile Length}}{\text{Hair Weight}}$ ratio scale × 100.

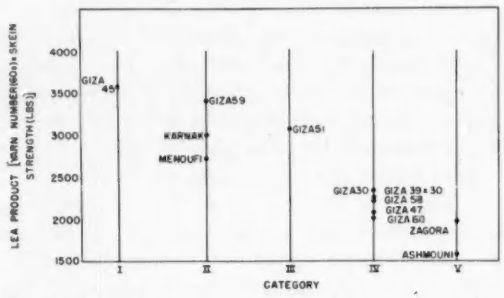


**Fig. 6.** Relation between yarn strength and category classification based on Suter-Webb data for Egyptian cottons.

tween the length/fineness ratio and yarn strength is clearly evident along with anomalously strong or anomalously weak classification of the cottons studied. If substitutes for the present commercial varieties of Egyptian cottons should be needed, Giza 59 stands out as a likely candidate for the position of Karnak, and Giza 51 for the vacant category once occupied by Giza 7. In Category IV, Giza 47 and Giza 58 are candidates for the position of Giza 30, while Giza 60 might take part in the Ashmouni category. Giza 39×30 is considered a better candidate for Ashmouni than for Giza 30. Although these observations are based on limited evidence, they are in general agreement with those of Youssef and Hafez [7].

## Acknowledgments

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# Letters to the Editor

## A Note on the Determination of Crystallinity of Cotton Fiber by Iodine-Adsorption Method

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August 29, 1956

To the Editor
TEXTILE RESEARCH JOURNAL

*Dear Sir:*

It is well known that the proportion of crystalline and amorphous regions in a fiber does play an important role in regard to its physical and chemical properties. Several techniques, both physical and chemical, have been developed for the determination of the crystalline-amorphous ratio. However, all these methods have been employed to show the differences in crystallinity between cottons treated differently, for example, mercerized cotton, degraded cottons, rayons, and other fibers, but no attempt seems to have been made to detect the difference in crystallinity between one cotton and another in the raw state. The chemical methods are based on the fact that the chemical reagents have ready access only to the amorphous region. Recently Hessler and Power [1] have employed Schwertassek's iodine-adsorption method, with slight modification, for the determination of the changes in crystallinity of cotton brought about by heat and chemical action. They also claim that "for the first time, it has been possible to demonstrate cellulose crystallinity differences due to fibre development as measured by fibre fineness and maturity." Therefore, in order to investigate this aspect further, and to find the suitability of this method for finding the differences in the crystallinity of different cottons, crystallinity was determined by this method with modifications to suit the local conditions.

Fifteen cottons belonging to different botanical species were selected for this experiment; these are given in Table I with some of their important fiber properties.

**TABLE I. Crystallinity Values as Obtained by Iodine-Adsorption Method**

| Sample No. | Cottons | Botanical species | Fiber length inches (mean) | Fiber weight $10^{-6}$ oz. per in. | Maturity* | | | Crystallinity of raw samples % | Crystallinity after wax extraction % |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | M. | H.M. | I. | | |
| 1 | 2 | 3 | 4 | 5 | 6 | | | 7 | 8 |
| (1) X5749 | Assam | G. Arboreum | 0.69 | 0.332 | 83 | 5 | 12 | 90.05 | 90.53 |
| (2) 12185 | Mollisoni | G. Arboreum | 0.74 | 0.265 | 77 | 6 | 17 | 88.91 | 89.97 |
| (3) 14060 | Gaorani 6 | G. Arboreum | 0.83 | 0.172 | 71 | 5 | 24 | 89.05 | 90.07 |
| (4) 14145 | Westerns | G. Herbaceum | 0.83 | 0.195 | 65 | 11 | 24 | 87.18 | 89.71 |
| (5) 13709 | Virnar | G. Arboreum | 0.87 | 0.191 | 77 | 5 | 18 | 87.82 | 89.97 |
| (6) 14075 | Nandyal 14 | G. Arboreum | 0.88 | 0.168 | 70 | 7 | 23 | 87.92 | 89.50 |
| (7) 13978 | Vijay | G. Herbaceum | 0.92 | 0.159 | 58 | 7 | 35 | 87.90 | 89.91 |
| (8) 14091 | Cambodia Co. 2 | G. Hirsutum | 0.92 | 0.148 | 51 | 6 | 43 | 88.88 | 89.99 |
| (9) 14195 | Jayadhar | G. Herbaceum | 0.93 | 0.191 | 73 | 4 | 23 | 87.86 | 90.00 |
| (10) 14061 | Laxmi | G. Hirsutum | 0.94 | 0.133 | 58 | 7 | 35 | 88.63 | 90.23 |
| (11) 14228 | M.C.U. 1 (Summer) | G. Hirsutum | 0.98 | 0.133 | 61 | 11 | 28 | 88.61 | 89.86 |
| (12) X7296 | Mwanza | G. Hirsutum | 1.08 | 0.139 | 41 | 14 | 45 | 90.10 | 90.60 |
| (13) X7298 | Sudan | G. Barbadense | 1.20 | 0.125 | 71 | 8 | 21 | 87.83 | 89.32 |
| (14) X7297 | Karnak | G. Barbadense | 1.26 | 0.107 | 76 | 5 | 19 | 89.35 | 89.43 |
| (15) M1880 | Sea Island | G. Barbadense | 1.40 | 0.081 | 54 | 8 | 38 | 88.31 | 89.32 |

* M. = Mature, H.M. = Half Mature, and I. = Immature.

Well-cleaned cotton was conditioned at 65% R.H., and 0.3 g. was weighed accurately. The method adopted was the same as that used by Hessler and Power. As the temperature was found to affect the iodine adsorption, the estimations were carried out at a constant temperature of 20° C. ± 1°. Closed bottles were used for the reaction, and these were kept inside the refrigerator, maintained at 20° C., for 1 hr. The exact amount of sodium sulfate which would give a saturated solution at 20° C. was dissolved in water, and the solution was brought to the required temperature prior to adding it to the cotton wetted with iodine solution.

The crystallinity values obtained are given in column 7 of Table I, each being an average of 8 estimations.

It will be noticed from these results that the crystallinity varies from 87.18 for Westerns to 90.10 for Mwanza, with a range of 3% only. Moreover, there is no definite relationship shown between the crystallinity percentage and the physical characteristics of the cotton fiber, viz., fiber length, fineness, and maturity.

In order to eliminate the effects of waxes on the adsorption of iodine by cotton, the same cotton samples were dewaxed by Soxhlet Extraction with benzene-alcohol mixture (1 : 1) for 6 hr. The crystallinity of dewaxed cottons was determined in the same manner and the values obtained are given in column 8 of Table I. These results indicate that the range of values becomes smaller, being 89.32 for Sea Island and 90.60 for Mwanza cotton, and also that no relationship exists between the percentage crystallinity and the physical characteristics. It thus appears that the crystallinity percentage determined by this method does not show significant differences between cottons in the raw state.

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# The Cyanoethylation of Wool

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September 11, 1956

To the Editor
TEXTILE RESEARCH JOURNAL

*Dear Sir:*

As an extension of our work on the cyanoethylation of natural polymers [2], we have investigated the cyanoethylation of wool. Recently, McPhee and Lipson [3] reported the reaction of acrylonitrile with wool in aqueous medium both before and after treatment to reduce the disulfide linkages to the dithiol. When we attempted cyanoethylation of unreduced wool by a similar procedure, it was found that a measurable degree of reaction could be obtained only under conditions which resulted in considerable damage to the wool by the alkaline catalyst.

We have now succeeded in introducing significant amounts of cyanoethyl groupings into wool without adversely affecting the physical appearance and properties of the fiber. In our procedure, wool was treated with a large excess of acrylonitrile and a small amount of aqueous alkali, whereas McPhee and Lipson operated with a small amount of acrylonitrile dissolved in a comparatively large quantity of basic solution [3].

A typical procedure, as carried out in our modified one-package dyeing machine [2], was as follows. Wool, in either yarn or fabric form, was steeped for 10 min. at room temperature in dilute sodium hydroxide solution of less than 0.4% concentration. The excess alkali solution was removed and the wet wool then treated at about 60° C. for about 1 hr. with sufficient acrylonitrile to fill the 6-liter kier system. The reaction mixture was neutralized with dilute acetic acid, and the wool washed with water and dried. In this way up to 5% by weight of cyanoethyl group-

**TABLE I. Conditions of Cyanoethylation**

| Run | Material | % NaOH | % Wet pickup | Time, min. | Temp., °C. | % N Increase | % Cyanoethyl | Appearance |
|---|---|---|---|---|---|---|---|---|
| A | Yarn* | 0.12 | 208 | 60 | 60 | 0.62 | 2.4 | Unchanged |
| B | Yarn | 0.40 | 179 | 60 | 60 | 1.30 | 4.9 | Somewhat yellow |
| C | Fabric† | 0.15 | 209 | 60 | 60 | 0.87 | 3.3 | Unchanged |
| D | Fabric | 0.15 | 169 | 30 | 65 | 0.71 | 2.7 | Faint yellowing |
| E | Fabric | 0.10 | 170 | 45 | 60 | 0.40 | 1.5 | Unchanged |
| F | Yarn | — | — | 60 | 75 | 0.17 | 0.6 | Unchanged |

* 42/2 worsted yarn.
† 8-oz. flannel.

**TABLE II. Properties of Cyanoethylated Wool ***

| Sample | Tensile strength, g. | | Tenacity | | Elongation, % | | Moisture regain, % |
|---|---|---|---|---|---|---|---|
| | Dry | Wet | Dry | Wet | Dry | Wet | |
| Control | 410 | 290 | 1.0 | 0.7 | 14.0 | 46.0 | 11.7 |
| Run A | 385 | 305 | 0.9 | 0.7 | 15.5 | 49.5 | 10.9 |
| Run B | 365 | 215 | 0.9 | 0.5 | 13.0 | 56.0 | 10.1 |

* Determined at 21° C. and 65% relative humidity.

ings were introduced, as determined by the increase in nitrogen content of the wool (Table I).

In the absence of alkali, the degree of reaction was considerably smaller (run F), since only such highly reactive groups as free amino groups would be substituted under these conditions [1]. With the catalyst other sites, such as amide nitrogen, apparently became available.

Some physical measurements have been carried out on this cyanoethylated wool (Table II). Measurements of tensile strength, in particular wet tensile strength, showed that the limited amount of alkali in the system had caused no serious damage to the wool, except in the case of run B where the highest concentration of sodium hydroxide was used. This was confirmed by the generally unchanged appearance and hand of the fiber and by microscopic examination. It appears therefore that the physical properties we determined were not substantially altered by the cyanoethylation treatment.

On the other hand, preliminary experiments with several types of dyestuffs have indicated that the dyeability was significantly affected. Differences were noted when a cationic dye (Sevron Red L applied at pH 7.0 ± 0.2 using sodium formate) or a direct dye (Calcomine[1] Sky Blue FF Ex. Conc., C.I. 518, applied at pH 4.3 ± 0.4 using formic acid) was employed in competitive dyeing of treated and untreated material. In both cases, the cyanoethylated wool took on the dye more rapidly and finally had a shade about three times as deep as the untreated wool. The same effect, but to a lesser degree, was observed when an acid dye (Calcocid[1] Fast Red BL, Pr. #101) was applied by a conventional method or by a cuprous-ion technique, or when an acid premetallized dye (Calcofast[1] Wool Bordeaux RB Conc.) or a neutral premetallized dye (Irgalan Red 3G) was used in a conventional procedure.

Dyeing experiments were also made using wool which had been treated only with alkali, with acrylonitrile, or with an inert solvent to determine whether or not the altered dyeing characteristics were due solely to the presence of cyanoethyl groups in the molecule. In the case of the cationic dye, at least, this appeared to be true.

Further study of the cyanoethylation of wool is indicated.

[1] Trademark, American Cyanamid Co.

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# Observations Relating to Cortical Asymmetry in Wool

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To the Editor

TEXTILE RESEARCH JOURNAL

*Dear Sir:*

That crimped wool fibers exhibit bilateral cortical asymmetry is now well established [2, 4, 6]. The two cortical segments have been named ortho-cortex and para-cortex.

The author has observed that ortho- and para-cortex can be distinguished in whole, untreated crimped fibers, under ordinary conditions of transmitted light microscopy. Figure 1*a* shows a fiber immersed in water, and Figure 1*b* shows a water-saturated fiber immersed in paraffin oil. The para-cortex, which is the segment on the inside of the curve, is characterized by many striations of about 20–30 $\mu$ in length; similar striations are infrequently seen in the ortho-cortex, where the most commonly observed structure is much smaller. If the cortical segments lie one on top of the other as viewed through the microscope, one can readily determine which segment is above and which below, by focussing up and down. Water saturation is not essential to the observation, but the higher the regain, the easier it is to distinguish the two segments.

*Configuration of Cortical Segments in Fibers*

The ability to distinguish the two cortical segments without staining enables their arrangement in untreated fibers to be investigated.

Ten Merino fibers, 2 to 3 in. in length, were examined, and it was found that the ortho- and para-cortex are not wound round each other in the same sense from end to end of a fiber. No regular arrangement was found. From end to end of a fiber, there may or may not be a net twist of the cortical segments; net twists varying from zero to six or seven turns have been seen. Fibers which had been relaxed by heating in water at 50° C. showed no more regularity in this respect.

*Supercontracted Wool*

Examination of fibers in the water-saturated state revealed that after crimped fibers had been irreversibly supercontracted, by heating in lithium bromide solution, the para-cortex was on the outside of the crimp wave instead of the inside as in untreated wool. It is reasonable to suppose that this occurs because the ortho-cortex has supercontracted more than the para-cortex. Curvature reversal of this kind was observed by Fraser and Rogers [3] on immersing Merino fibers in alkaline thioglycollate solution, and has been suggested by Dusenbury and Jeffries [1]

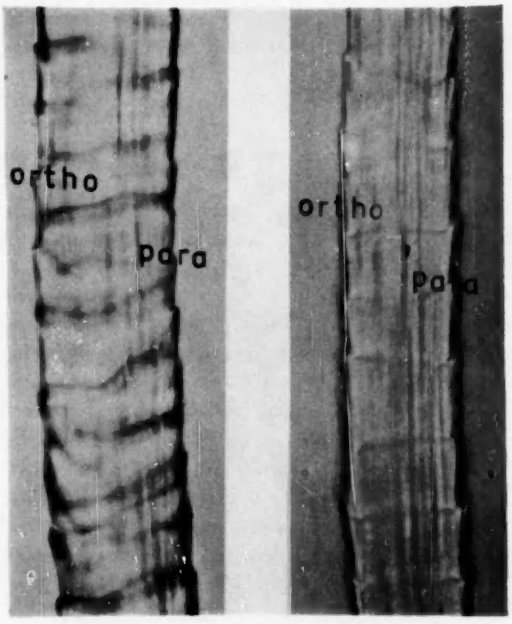


**Fig. 1.** Micrographs showing the difference in appearance of ortho- and para-cortex in water-saturated Merino wool fibers. *a*, Fiber in water. Striated para-cortex on inside of curve. *b*, Water-saturated fiber in paraffin oil.

as the reason why Horio and Kondo [4] concluded that the para-cortex was preferentially stained by Ponceau 2R.

In addition it was found that these supercontracted fibers take up methylene blue dye (0.16 *W/V* methylene blue in a phosphate buffer at pH 5.5) at room temperature, and that, as in normal wool, the ortho-cortex is more heavily dyed than the para-cortex.

*Wool from Copper-Deficient Sheep*

When sheep which normally grow crimped wool are fed a copper-deficient diet they produce "steely" wool having no definite crimp. Since bilateral structure of the fiber cortex is usually associated with crimp, it is of interest to examine this wool. One of the wools used was from a sheep which, for several months, was on a copper-deficient diet, and which was then given a copper supplement. Some 7 cm. of the wool was typically steely, and this was followed by about 4 cm. of apparently normal wool, with well-defined crimp. When the steely part of the fibers was examined, in the water-saturated state, under the microscope, no bilateral structure could be seen, whereas in the normal part of the same fibers, the two segments could readily be distinguished.

Now Fraser and Rogers [2] have reported that their staining methods showed differentiation in steely wool, but that the differentiation was not as distinct as in normal wool. Since different levels of copper deficiency are possible, it was thought that bilateral asymmetry might be lost when the deficiency is sufficiently serious. In an attempt to determine whether or not this had occurred in the above-mentioned sample, locks of the wool were dyed in 0.16% *W/V* methylene blue, for 30 min. at 100° C., at pH's varying between 3.5 and 7.5. In all cases the steely wool dyed more heavily than normal wool in the same lock. On sectioning the fibers in a Hardy microtome, it was found that in every case the normal wool showed clear bilateral asymmetry of dyeing, whereas in no case did the steely wool show this phenomenon. Usually steely wool was characterized by lightly dyed or undyed spots distributed over the sections.

Later it was found that a dyeing technique (Coomassie Violet dye) due to Simmonds (unpublished data) of the Biochemistry Unit of these laboratories indicated the presence of two cortical segments in this steely wool. Furthermore segmentation can be seen in the same wool during treatment of cross sections, or whole fibers, with a solution made up of KOH 2 g., water 2 ml., and ethanol 96 ml. The ortho-cortex is attacked first, and after times varying between 30 min. and 2 hr., segmentation can be seen easily.

Other steely wool samples yielded similar results.

It is clear therefore that the loss of crimp, the different appearance under the microscope, and the different dyeing properties of steely wool are not due to loss of bilateral cortical asymmetry. It must be that in steely wool the physical and chemical properties of ortho-cortex are less different from those of para-cortex than is the case in normal wool.

Another sample used in this investigation was from a "black" Merino sheep which had suffered, intermittently, varying levels of copper deficiency, (In a "black" sheep copper deficiency causes loss of both pigment and crimp.) At the tip of the staple was a band of nearly white wool; then followed dark brown, nearly white, dark brown, and light brown bands. These bands indicated, successively, a serious copper deficiency, no deficiency, serious deficiency, no deficiency, and a moderately serious deficiency. A lock of this wool was dyed in methylene blue, and sections were cut at the light brown band, and at the central, nearly white band. Examination of the former sections (slight deficiency) showed that many fibers, including almost all the ones of larger diameter, were heavily pigmented; many fibers were lightly pigmented; and very few were without pigment. In the case of heavily pigmented fibers, there was no obvious asymmetric distribution of pigment, but in lightly pigmented fibers, it was very clear that the pigment was preferentially laid down in the para-cortex (see Laxer and Whewell [5]). All the fibers showed clear bilateral asymmetry of dyeing.

Of sections cut in the central, nearly white, band, about 50% (again including nearly all the fibers of larger diameter) were so heavily pigmented that no bilateral asymmetry of pigmentation could be seen, about 20% were lightly pigmented (often with only two or three spots of pigment in the para-cortex) and 30% were unpigmented. Of the unpigmented fibers, about 70% showed no clear bilateral asymmetry of dyeing, but instead had scattered undyed spots such as were seen in the above-mentioned white, steely wool.

It must be concluded that methylene blue dyeing, without some pretreatment such as peracetic acid oxidation [2], is not a reliable method of detecting cortical asymmetry in wool from copper-deficient sheep.

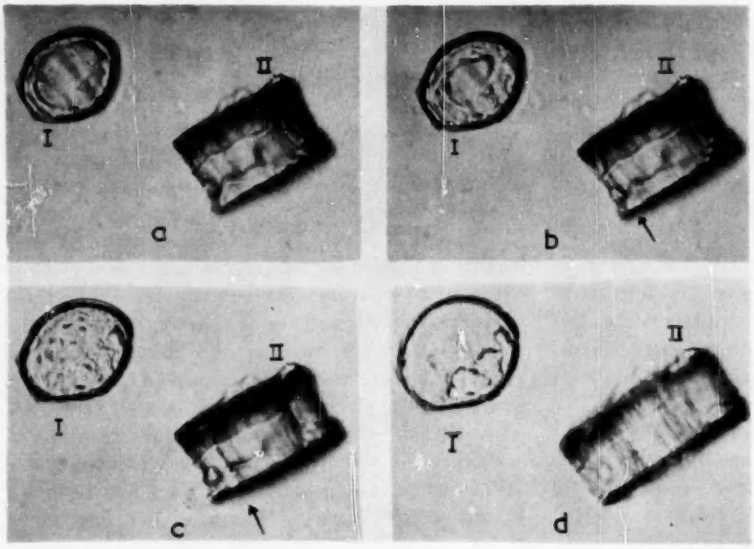


**Fig. 2.** Micrographs showing the penetration of wool by ethanolic KOH. *a*, Sections, initially about 28 $\mu$ and 41 $\mu$ in diameter, after 17 min. in reagent at 17° C. Penetrating front can be seen in I. *b*, Same sections as in *a*, but after 29 min. Penetrating front can be seen in I, and in one side of II. *c*, Same sections as in *a*, but after 37 min. Penetration is very nearly complete in I. The position of the penetrating front in II is indicated. *d*, Same sections as in *a*, but after 60 min. Bilateral structure apparent in I. The para-cortex is the smaller segment.

*Penetration of Wool by Ethanolic KOH*

When a wool fiber with bilateral cortical structure is immersed in a solution containing KOH 2 g., water 2 ml., and ethanol 96 ml., and observed under the microscope, it can be seen that both ortho- and para-cortex are penetrated by the reagent. Later it becomes obvious that the ortho-cortex is preferentially attacked, and bilateral structure is easily seen. There is no curvature reversal.

The progress of events was readily followed by observing cross sections. Sections were cut and mounted in the reagent, on a microscope slide, under a cover slip which was sealed down with silicone grease to prevent evaporation. Photographs *a*, *b*, and *c* of Figure 2 show the advancing front of penetrant approaching the axis of Section I, and in Figure 2*d*, bilateral structure is apparent in this section. Partly because the microscope was focussed on Section I, penetrating fronts are less easily seen in Section II, which appears in profile, but where they can be seen, they are indicated by arrows, and dots spaced along the fronts. No evidence was found that penetration proceeds appreciably faster in one segment than in the other.

It is interesting to note that, even with these short sections, the penetrating fronts proceed radially, showing that diffusion in the axial direction is unimportant.

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A. R. HALY

# Acetone from Simple Sugars

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To the Editor

TEXTILE RESEARCH JOURNAL

*Dear Sir:*

In connection with our work on hemicelluloses of jute fiber, we were looking for a suitable method for the estimation of rhamnose in the presence of xylose, arabinose, galactose, etc. Marshall and Norris [2] confirmed the presence of acetone in the acid distillate of rhamnose (they did not estimate it) and considered it as the principal interfering substance in the estimation of rhamnose. No reference was available in literature about other simple sugars giving acetone on distillation with 12% HCl; it was considered worth while to see if rhamnose could be estimated from the acetone it liberates. As a preliminary step, pure samples of xylose, arabinose, and glucose were distilled with 12% HCl, as in the determination of furfural, and acetone was detected in the distillate in every case by the iodoform test as well as with *o*-nitro-benzaldehyde. On distillation with 2% NaOH also, they, as well as rhamnose, gave acetone. Acetone was colorimetrically estimated by salicylic aldehyde according to the method of Csonka [1] (which is specific for acetone) as modified by Ravin [3] with a Spekker Photoelectric Absorptiometer; the values are given in Tables I and II. Except arabinose, others give appreciably larger amounts of acetone on alkali distillation than on acid distillation. As the yield of acetone is quite small, it accounts only partly for the discrepancy between the theoretical and actual yields of furfural (or methylfurfural) from these sugars.

Liberation of acetone from jute fiber on acid distillation (Table III) seems to be preceded by the hydrolysis of cellulose or hemicellulose to simple sugars inasmuch as on alkali distillation, the fiber yields practically no acetone. Sanyal [4] recently obtained iodoform in the distillate of jute and its constituents. Acetone may, in part, be responsible for this.

**TABLE I. Acetone from Sugars Distilled with 12% HCl**

| Sugars | % Acetone |
|---|---|
| Rhamnose | 0.336 |
| Arabinose | 0.272 |
| Xylose | 0.120 |
| Glucose | 0.037 |

**TABLE II. Sugars Distilled with 2% NaOH**

| Sugars | % Acetone |
|---|---|
| Rhamnose | 0.835 |
| Arabinose | 0.230 |
| Xylose | 0.276 |
| Glucose | 0.304 |

**TABLE III. Acetone from Jute**

| Raw jute | % Acetone |
|---|---|
| Distilled with 12% HCl | |
| Olitorius | 0.077 |
| Capsularis | 0.080 |
| Distilled with 2% NaOH | |
| Olitorius | 0.006 |
| Capsularis | 0.004 |

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# Book Review

**A Technology for the Analysis, Design, and Use of Textile Structures as Engineering Materials (Edgar Marburg Lecture).** Walter J. Hamburger. Philadelphia, American Society for Testing Materials, 1956. 50 pages. Price $1.50 to nonmembers, $1.15 to members of the Society.

The Marburg Lecture honors and perpetuates the memory of Edgar Marburg, first Secretary of the American Society for Testing Materials. Its purpose is to have described at the annual meeting of the Society, by leaders in their respective fields, outstanding developments in the promotion of knowledge of engineering materials. The 1955 Lecture was presented by Walter J. Hamburger before the fifty-eighth annual meeting of the Society, June 29, 1955, Atlantic City, New Jersey.

In the first Marburg lecture which had to do with textiles, "Textile Fibers, an Engineering Approach to their Properties and Utilization," Harold DeWitt Smith, in 1944, set up a framework for a systematic engineering approach to an understanding of textile fibers as engineering materials. He illustrated his discussion with data which had become available up to that date, comparing the properties and behavior of the various fibers for textile use. Since Dr. Smith's lecture much progress has been made and a great deal of information published in all areas examined by Smith and in those recommended for study. It is in the light of present-day accumulated knowledge that Dr. Hamburger has termed his treatise in the main "a philosophical discussion." It is a "philosophy" based on the findings of research, for the details of which the reader is referred to a comprehensive list of references to the published literature with which the treatise is fully documented. The basis of the philosophy is that textiles can be designed to meet specific end-use requirements.

Following a few introductory pages, the material properties which are desirable in fibers, yarns, and fabrics are described, and the many factors which affect their translation into structures are described in detail. Of these factors, structural geometry is shown to be the most important. The influence of shape factors and the interaction of such strains as bending, compression, shear, tension, and torsion are considered. Suggestions as to the direction of future research are given. Forty-eight references are cited, and in addition, there are seven pages of selected pertinent references.

This treatise will be valuable for reference for those persons actively working in the field. Newcomers to textile research and students will find nowhere else so comprehensive a coverage of the problems to be met with and progress to date in the development of improved textiles.